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HYDROTHERMAL ROCK ALTERATION AT WAIRAKEI, NEW ZEALAND.

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CONTENTS.

	PAGE
Abstract	1
Introduction	1
Stratigraphic sequence and description of rocks	3
Hydrothermal alteration:	
Zone of sulfuric acid leaching	5
Zone of argillization	5
Zone of zeolitization	6
Zone of feldspathization	6
Results of chemical analyses	7
Prevailing temperature and chemical environment:	
Formation of kaolinite, opal, and alunite	9
Formation of montmorillonite type of clay	10
Introduction of ptilolite	11
Replacement of plagioclase by adularia	12
Conclusions	13
Bibliography	13

ABSTRACT.

Exploratory drilling at Wairakei reveals that hydrothermal reagents have altered flat lying tuffaceous and arenaceous rocks but not the interbedded argillaceous rocks. Four zones of progressive alteration can be distinguished. A superficial zone of sulfuric acid leaching is followed at depth by a zone of argillization. On the zone of argillization is superimposed a zone of zeolitization at shallow depth and a zone of feldspathization lies at deeper levels. No evidence has been found that the drill holes penetrated into the zone of primary acid leaching, which is expected to occur below the zone of feldspathization. Temperatures at which montmorillonite-like minerals, ptilolite and adularia form are given, and the chemical character of the environment prevailing during the formation of these minerals is elucidated.

INTRODUCTION.

The Wairakei thermal area with many active hot springs and fumaroles is located in the volcanic region in the central part of the North Island, approximately four miles in a north-north-easterly direction from Lake Taupo.

The geology of this region was described in detail by Grange (7).[1] At present, as part of the investigation to test the possibility of obtaining geothermal steam, a number of drill holes, some to 1,500 feet in depth have been drilled along a line (D-line) crossing the area in a north-westerly direction (Fig. 1).

The purpose of this paper is to describe the results of petrological studies of drill cores undertaken as part of the geothermal investigation.

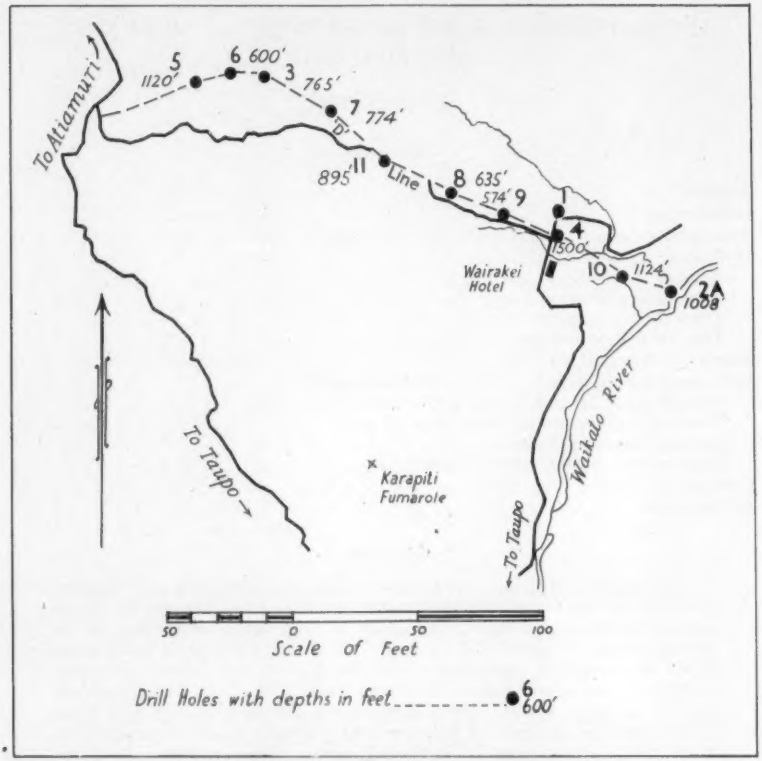

FIG. 1. Locality map of drill holes on D-line at Wairakei.

Acknowledgments.—Acknowledgment is made of the assistance of Mr. T. A. Rafter, Dominion Laboratory, for the chemical analyses of the rocks; of Mr. C. T. Banwell, Dominion Physical Laboratory, for making available the results of his temperature measurements, and of Mr. Fieldes, Soil Bureau, for X-ray examination of clays.

[1] Numbers in parentheses refer to Bibliography at end of paper.

STRATIGRAPHIC SEQUENCE AND DESCRIPTION OF ROCKS.

The stratigraphic sequence of rocks is summarized in Table 1, which shows that the tuffaceous rocks occurring between the recent cover and the Huka Formation in the western part of D-line are absent in the eastern part where diatomaceous mudstones and siltstones are developed. The correlation of cores shows that the beds are lying flat.

The recent cover consists of clay, and pumiceous and rhyolitic sands and gravel, in places slightly indurated.

The light grey or creamy colored Upper and Lower Wairakei lapilli tuffs have the composition of a plagioclase rhyolite. The phenocrysts in decreasing order of abundance are andesine plagioclase, quartz, hypersthene, and hornblende. Magnetite and rare apatite are accessory minerals. The groundmass consists of glass shards and pumiceous shreds and lapilli; the latter having a maximum diameter of 2 inches. In places, round or eliptical bodies of 10 mm maximum diameter and consisting of minute rhyolitic glass fragments

TABLE 1.

STRATIGRAPHIC SEQUENCE OF ROCKS ON D-LINE.

	West, drill holes 3, 5, 6, 7, 8, 9, 11	East, drill holes 2, 4, 10
	Thickness in feet	
Recent cover	0–240	0–240
Upper Wairakei lapilli tuff	115–231	Absent
Chalazoiditic vitric tuff	0–4	Absent
Lower Wairakei lapilli tuff	81–280	Absent
Altered chalazoiditic vitric tuff	3–30	Absent
Diatomaceous mud- and siltstones	Absent	200–240
Huka Formation	197 to 729 (Total thickness not known)	

and crystal debris, are scattered throughout the rock. For these bodies Berry (4) suggested the name chalazoidite.

The chalazoiditic vitric tuff which separates the Wairakei lapilli tuff into an upper and lower sheet, and the altered chalazoiditic tuff which overlies the Huka Formation are petrographically similar rocks. Both are made up of numerous chalazoidites embedded in a matrix consisting of the same material as the chalazoidites.

The diatomaceous mudstones and siltstones occurring only in the eastern part of D-line consist of clay and a small amount of detrital oligoclase, quartz, and minute shreds of rhyolitic glass. Ferromagnesian minerals are rare. The clay appears to be a mixture of montmorillonite-like minerals and kaolinite. Pyrite is not common in these rocks, which generally contain carbonaceous material and numerous diatoms.

The Huka Formation consists of a series of sedimentary rocks comprising claystones, mudstones, and siltstones interbedded with various vitric tuffs and tuffaceous and pumiceous sandstones. The argillaceous rocks commonly show a fine and distinct lamination that can often be observed only under the microscope. Their dominant constituent is a platy montmorillonite-like min-

eral with a small amount of detrital plagioclase and quartz. Carbonaceous material is usually present. The thickness of the argillaceous rocks ranges from a few inches to 50 feet. The vitric tuffs are petrographically similar to the Upper and Lower Wairakei lapilli tuff. The tuffaceous sandstones consist of subangular to semirounded rhyolitic and pumiceous grains together with crystals and fragments of andesine or albite-oligoclase, quartz, and occasional pyroxene and biotite. Magnetite and rare apatite are accessory minerals. At higher levels pyrite is introduced.

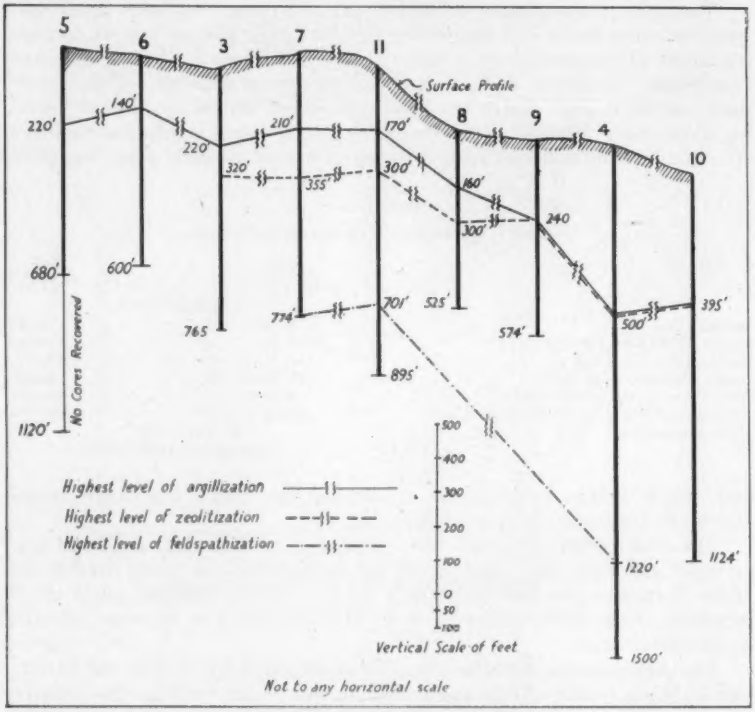

FIG. 2. Distribution of zones of alteration at Wairakei.

The pumiceous sandstones are made up of pellets of rhyolitic pumice generally containing phenocrysts of andesine plagioclase and corroded quartz. The interstices are filled with fragmental plagioclase and quartz, together with fine glassy material derived by attrition of pumice. Accessory constituents are ferromagnesian minerals, rare magnetite and apatite, and occasional diatoms. The arrangement of fragmental crystalline material round pumiceous pellets produces a characteristic texture.

HYDROTHERMAL ALTERATION AT WAIRAKEI.

Petrographic examination has shown that at Wairakei hydrothermal reagents have altered and are still altering tuffaceous and arenaceous rocks but not the interbedded argillaceous rocks, which are impervious. Although a few cores from almost every drill hole are fractured, extensive fissures that would allow the flow of a large volume of hydrothermal solutions have not been observed. The cores do not contain veins; and veinlets are rare.

When the distribution of the various types of hydrothermal alteration is studied, four main zones may be distinguished (Fig. 2). In order of progressive alteration with depth these zones are as follows:

A. Zone of sulfuric acid leaching.
B. Zone of argillization.
C. Zone of zeolitization.
D. Zone of feldspathization.

A. *Zone of Sulfuric Acid Leaching.*—In drill holes 3, 5, 7, 8, 9, and 11, the Wairakei lapilli tuff is weathered down to a maximum depth of 240 feet, but at and near the surface of drill hole 6 a sulfuric acid leaching zone has locally developed. It is marked by a suite of secondary minerals consisting of kaolinite, alunite, and opal. In the first 12 feet in depth this drill hole penetrated a layer of clay made up almost entirely of kaolinite, some crystals of which display the characteristic vermicular habit. A small amount of opal is present. Of the primary constituents only quartz phenocrysts survived. A few grains of leucoxene resulted from the alteration of titaniferous magnetite.

The cores between 12 and 20 feet are only partly kaolinized. Although the phenocrysts apart from quartz are altered to clay, some glass remains unaltered. Opal persists to a depth of 20 feet. From 20 to 70 feet all of the glass is completely isotropic but fresh plagioclase does not appear until a depth of 80 feet is reached. At 32 feet alunite makes its first appearance and persists to 50 feet. It forms minute lathes scattered throughout the rock and in the core at 40 feet it also replaces some glass shards. In this core pyrite has been detected.

Below 80 feet, montmorillonite-like clay and pyrite are the characteristic hydrothermal minerals. However, the appearance of siderite at 90 feet is significant; it shows that a profound change occurred in the character of the hydrothermal alteration. It is also evident that the formation of kaolinite, opal, and alunite is only a superficial feature.

B. *Zone of Argillization.*—The most common hydrothermal alteration noted on D-line is the conversion of glass, particularly of pumiceous shreds and lapilli, into clay minerals of the montmorillonite group. This argillization has affected all tuffaceous and arenaceous rocks penetrated by the drill holes, and superimposed on it are the other more progressive alterations—the zeolitization and feldspathization.

In handspecimen the argillized pumice is mostly of deep olive-green color and when seen under the microscope the clay forms minute light to dark green scales generally arranged approximately parallel to and along the drawn out

vesicules of the pumice. This parallel arrangement produces an aggregate optical orientation. In places the clay shows faint pleochroism and radiated or spherulitic structure. The montmorillonite-like clay shows comparatively high birefringence and its indices of refraction vary from $\beta = 1.539$ to 1.624. Results of an X-ray examination by Fieldes have confirmed the optical identifications.

The argillization is associated at high levels, particularly in the Wairakei lapilli tuff, with the introduction of pyrite. This mineral occurs invariably in crystals with cubical and octahedral faces and in this respect it can be contrasted with the pyrite of different origin, which exhibits pyritohedral crystal faces and is associated with carbonaceous material in mudstones of the Huka Formation.

Plagioclase has not been affected by argillization, but locally in drill holes 3 and 6, replacement by calcite has been noted. The ferromagnesian minerals are altered to clay in drill holes 3, 5, 6, and 7, but remain unaltered at corresponding levels in drill holes 4, 8, 9, 10, and 11. Quartz is always unaltered.

C. *Zone of Zeolitization.*—The zeolite mineral ptilolite [2] is the characteristic hydrothermal mineral of the zeolitization zone. The distribution of ptilolite is shown in Figure 2 where it can be seen that in general the zone of zeolitization is superimposed at deeper levels on the zone of argillization. Ptilolite in aggregates of cottony fibres showing a radiated structure (Fig. 3) fills rock pores and vesicles in the pumice. From the fact that the vesicles in the argillized pumice are filled with fresh ptilolite it can be inferred that the argillization preceded the deposition of zeolite which is often accompanied by the introduction of secondary quartz.

Another zeolite mineral, probably analcite, is in some drill holes associated with ptilolite; it forms minute beads filling the pores and lining the walls of the larger cavities. These beads commonly form kernels of the cottony ptilolite aggregates (Fig. 3). Less common is the zeolite heulandite which has been identified in two or three cores.

Ptilolite has not been found in drill holes 5 and 6 but instead a small amount of secondary albite and quartz is present. This minor introduction of albite should not be confused with the more intense and widespread formation of adularia described in the following section on feldspathization.

D. *Zone of Feldspathization.*—At greater depth the zone of zeolitization is followed by the zone of feldspathization characterized by the presence of a secondary potash feldspar, adularia (Fig. 2). This feldspar, commonly containing wisps of sericite, has been identified in tuffaceous and arenaceous rocks in drill holes 4, 7, and 11. The formation of adularia is generally limited to the replacement of plagioclase and in one single thin section, all stages of replacement can be seen (Fig. 4). An exception is the core at 701 feet in drill hole 11 where an abundance of tiny euhedral crystals of adularia are embedded in the argillized glass and clayey cement of a tuffaceous sandstone.

The replacement of adularia is generally associated with the development of titanomorphite, minute granules of which are scattered throughout the rock

[2] Optical, chemical, and X-ray data are being published elsewhere.

and rarely enclose remnants of titaniferous magnetite. Secondary quartz is another common hydrothermal mineral accompanying the formation of adularia. Prehnite, probably of hydrothermal origin, has been identified in one of the cores from drill hole 11 containing adularia and titanomorphite; the vertical range is less than 23 feet.

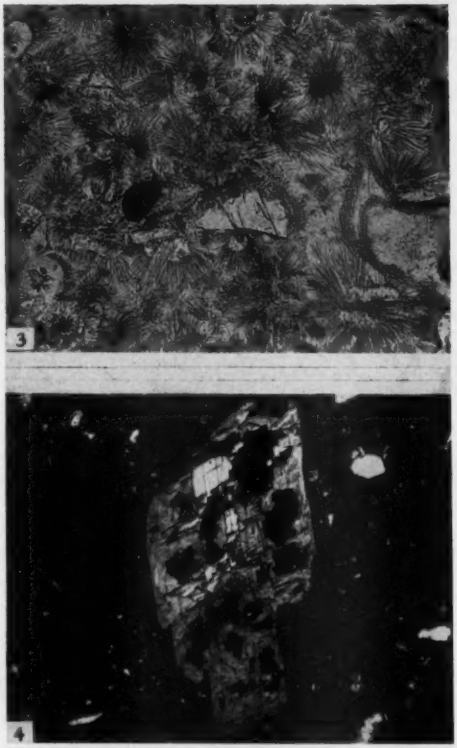

FIG. 3. Photomicrograph of tuffaceous sandstone from drill hole 11, at 419 feet, showing cottony aggregates of ptilolite; some contain a kernel of analcite. Ordinary light × 120.

FIG. 4. Photomicrograph showing a soda-lime plagioclase in pumiceous sandstone from drill hole 11, at 757 feet. The plagioclase is largely replaced by adularia. White patches are remnants of plagioclase; surrounding light grey area is adularia; black patches are holes in the section. X-nicols, × 25.

RESULTS OF CHEMICAL ANALYSES.

One core from each of the zones of argillization, zeolitization and feldspathization has been analyzed and the results are shown in Table 2. These

tuffaceous and arenaceous rocks are made up of material that originally had the composition of a plagioclase rhyolite. As corresponding unaltered rocks are not available it may be valid to compare the altered rocks with an obsidian and ignimbrite occurring in the neighbouring area and having the composition of a plagioclase rhyolite. The analytical results are recalculated on a water-free basis.

In the analyzed core of the Wairakei lapilli tuff (No. 1) pumice is altered to montmorillonite type of clay and pyrite is introduced. In comparing it with the fresh rocks (Nos. 4 and 5), it can be seen that the altered rock lost an appreciable amount of soda. On the other hand, it gained a considerable amount

TABLE 2.

COMPARISON OF ALTERED AND UNALTERED ROCKS.

	No. 1	No. 2	No. 3	No. 4	No. 5
SiO_2	73.86	72.05	69.20	75.93	73.47
Al_2O_3	13.53	15.46	14.40	12.84	14.56
Fe_2O_3	1.35	0.48	0.58	0.34	1.75
FeO	1.53	1.47	2.19	1.07	0.66
TiO_2	0.37	0.34	0.51	0.21	0.29
MgO	1.28	0.84	0.58	0.22	0.24
CaO	2.22	2.93	1.00	1.45	1.36
Na_2O	1.61	1.87	0.93	4.00	4.31
K_2O	3.13	2.74	10.16	3.65	2.99
P_2O_5	0.09	0.15	0.08	0.02	0.09
MnO	0.16	0.06	0.10	0.05	0.09
BaO	0.04	0.10	0.07	0.13	0.11
ZrO_2	—	0.01	—	0.04	0.01
FeS_2	0.78	1.32	0.15	0.01	0.02
Cl	—	0.05	0.01	Trace	—
	99.95	99.87	99.96	99.96	99.95
H_2O lost above 105° C	4.06	6.30	0.97	0.35	1.18
H_2O lost below 105° C	2.76	4.48	0.14	0.04	0.44
Molecular ratio $\frac{Al_2O_3}{MgO}$	4.12			25.0	23.7

No. 1. Argillized Zone: Wairakei lapilli tuff from drill hole 5, at 230 feet.
No. 2. Zeolitization Zone: Tuffaceous sandstone with ptilolite from drill hole 11, at 419 feet.
No. 3. Feldspathization Zone: Tuffaceous sandstone with adularia from drill hole 11, at 701 ft.
No. 4. Fresh obsidian from Whakapoungakau Mountain, east side Lake Taupo (Grange 7).
No. 5. Fresh ignimbrite, Waihaha (Grange 7).

of magnesia, some lime and ferrous iron, and a small amount of titania. These introduced constituents together with combined water have been used for the formation of the clay. The analytical results do not indicate a change in silica and alumina.

The gain in magnesia deserves special attention as an excess of this base is an essential condition for the formation of the montmorillonite type of clay. An addition of magnesia to, or its subtraction from, the rock is particularly well indicated by the ratio of molecular proportions Al_2O_3/MgO, provided that the amount of alumina has not changed as is the case of specimen No. 1. The introduction of additional magnesia from an outside source is marked by

a decrease of this ratio as shown in Table 2 which contains the ratio of molecular proportions Al_2O_3/MgO of the Wairakei lapilli tuff (No. 1) and fresh silicic rocks (Nos. 4 and 5).

At present there is no evidence for introduction of additional magnesia by hydrothermal solutions which acquired an excess of magnesia by leaching more basic rocks at a greater depth. Neither is there any basis for postulating the introduction of magnesium by volatiles. The most probable explanation is that magnesium is introduced in the pore solutions by downward percolating surface water.

If the analytical results of the core No. 2 are compared with that of the fresh rocks, it can be seen that the altered rock gained similarly to the core No. 1, ferrous iron, titania, magnesia, and lime, as well as sulfur and water. The increase in phosphorus pentoxide is due to the presence of more apatite; a few crystals of this mineral have been occasionally observed concentrated in a small area of the thin section in association with ptilolite. This apatite is, perhaps, of hydrothermal origin. However, the chemical changes caused by the deposition of ptilolite are obscured as the rock was argillized prior to the introduction of the zeolite. Moreover, the introduction of ptilolite is feeble in comparison with the intense mineralogical changes produced by argillization and feldspathization.

The abundance of adularia in the analyzed core No. 3 is well demonstrated by the high potash content. Apart from a negligible amount of sericite, no other potash-bearing mineral is present. A conspicuous gain in ferrous iron and titania may also be noted whereas magnesia has been introduced in a lesser degree. The replacement of soda and lime in the plagioclase is shown by the small amount of these constituents. The deficiency in silica in spite of the formation of a more siliceous feldspar, thus requiring an introduction of silica, suggests that the rock was intensely leached prior to its alteration by hydrothermal solutions. Compared with the specimens Nos. 1 and 2 water is present in a small amount. It appears that the greater part of the water taken up during the argillization has been later freed and displaced from the rock during the formation of adularia.

PREVAILING TEMPERATURE AND CHEMICAL ENVIRONMENT.

Formation of Kaolinite, Opal, and Alunite.—The association of kaolinite and opal with alunite indicates that the formation of this mineral suite is due to sulfuric acid solutions. At present H_2S is escaping from the ground in the vicinity of drill hole 6 and sulfur is being deposited on the surface. As suggested by Allen and Day (1) sulfuric acid solutions form by the oxidation of H_2S vapors by oxygen entrained in the descending meteoric water. According to the temperature measurements carried out by Banwell,[3] the prevailing temperatures in drill hole 6 at a depth between 25 and 50 feet range from 46° to 58° C.

From the fact that the most intensely altered rock is restricted to a relatively small vertical range down to 20 feet from the surface, it is inferred that

[3] Unpublished Departmental Report, D. P. L. No. 8/7/149.

the acidity of the solutions decreases with depth. Further, it appears that the alteration is either effected by weak sulfuric acid solutions or the alteration has been going on for a relatively short time. Perhaps both factors should be considered equally. The first appearance of pyrite at 40 feet suggests that the mineral does not favor a strongly acidic environment. This is in agreement with the result obtained by Allen and co-workers (3) who synthesized pyrite.

The presence of siderite at 90 feet is good evidence of a change in chemical conditions at this depth, as siderite is not stable in sulfuric acid solutions. The change in the chemical environment is mineralogically manifested by the complete absence of kaolinite, opal, and alunite below 80 feet in depth. It is in some way obscured by a narrow zone between 80 and 139 feet where old weathering and hydrothermal alteration by neutral to alkaline pore solutions overlap. However, at depth greater than 139 feet, neutral to alkaline pore solutions are active only under such conditions as will be explained below. Thus, the sulfuric acid solutions are gradually, as depth increases, neutralized by ascending alkaline solutions.

Formation of Montmorillonite Type of Clay.—The absence of fractures through which hydrothermal solutions could rise suggests that the reagents

TABLE 3.

TEMPERATURES MEASURED AT THE HIGHEST LEVEL OF ARGILLIZATION.

Drill hole	3	4	5	6	7	8	9	10	11
Highest level of argillization in feet	220	500	220	140	210	160	240	395	170
Temperature, ° C	56	164	20	113	26	134	158	107	128

which brought about the argillization of the glass, and the minor associated mineral changes, ascend through the pores of the rock. Water vapors of low temperature accompanied by a small amount of H_2S gas escape from hydrothermal solutions active at greater depth; they ascend through the pores and meet at higher levels downward percolating surface water. Thus, the pore solutions resulting from the interaction of the ascending volatiles and the descending surface water effect the argillic alteration; they are expected to be of low temperature. In Table 3 are listed the actual temperatures measured by Banwell [4] in the drill holes at a depth corresponding to the highest level of argillization. This table shows a great variation in the prevailing temperature and indicates that the temperature may be as low as 20° C. This seems to agree with observations made by Ross and Hendricks (10) who state that montmorillonite-like minerals are stable over rather a wide range of temperature and that these clay minerals have formed by pure weathering and by low temperature hydrothermal processes. However, Fenner (6) reported that in Yellowstone Park, beidellite is now forming from feldspar at 205° C, at a depth of 246 feet, under alkaline conditions. According to Brannock and

[4] Op. cit., p. 9.

co-workers (5) in Steamboat Springs, Nevada, an alteration suite comprising montmorillonite-beidellite clays, zeolites, and serpentine, is formed in mildly alkaline waters at 95° C.

The association of pyrite with argillized glass shows that pyrite was introduced by the same hydrothermal fluids that caused the argillic alteration. This association indicates as pointed out by Fenner (6), and Ross and Hendricks (10), that the clay formed under the reducing conditions of neutral to alkaline pore solutions. This is confirmed by the results obtained by Wilson,[5] who analyzed water yielded by some of the drill holes. Alkaline to neutral pore solutions of low temperature as well as the mineralogical and chemical changes produced by them are indicative of hydrothermal conditions that would be expected in the outermost zone of the meteoric water shell in a fumarolic and hot springs area.

Introduction of Ptilolite.—An excess of soda and lime must be present in hydrothermal solutions depositing ptilolite, which is essentially a soda-lime zeolite but also contains some potash. The enrichment of the solutions in soda and lime is effected by base exchange at greater depth in the zone of feldspathization where a soda-lime plagioclase is replaced by a potash feld-

TABLE 4.

TEMPERATURES MEASURED AT THE HIGHEST LEVEL OF ZEOLITIZATION.

Drill hole	3	4	7	8	9	10	11
Highest level of zeolitization in feet	320	500	355	265	240	395	300
Temperature, ° C	108	164	60	156	158	107	154

spar, and the released soda and lime are taken up by the solutions. The fact that the plagioclase is not altered in the rocks containing ptilolite points to alkaline solutions, which apart from being rich in soda and lime, contain an excess of silica. This agrees with the results of mineral synthesis, which show that plagioclase remains unaltered in alkaline solutions with an excess of silica, even at elevated temperatures. Lovering (9) stresses the fact that zeolites have been synthesized only in alkaline acqueous solutions and that the temperature in some cases was as low as 60° C.

The temperatures measured by Banwell[6] in the drill holes at the highest level of zeolitization are given in Table 4. These temperatures prevailing during the formation of ptilolite at Wairakei may well be compared with temperatures at which zeolites now form in other regions: Fenner (6) states that the zeolite heulandite forms from alkaline waters at 122° C down to 85 feet. Brannock and co-workers (5) reported the formation of zeolites in mildly alkaline solutions at 95.5° C in Steamboat Springs, Nevada.

According to Schmitt (11), alkaline hydrothermal solutions, with concentrations of soda, lime, and silica, and of comparatively low temperature, would

[5] Geothermal Chemical Report No. 3, Dominion Laboratory.
[6] Op. cit., p. 9.

form well away from the interface of the meteoric water shell and the magmatic emanations. Therefore, zeolites develop near the end of the reaction series of hydrothermal solutions.

Replacement of Plagioclase by Adularia.—The replacement of a soda-lime plagioclase by a potash feldspar leads to the inference that alkaline solutions containing a relatively large concentration of K + cations are active in the zone of feldspathization. The formation of a potash feldspar requires additional silica to be present in excess in these solutions. Thus, during the formation of adularia, potash, and silica from the solutions are fixed in the rock, whereas Na + and Ca ++ cations are freed and acquired by the solutions. Some of the lime released is reassembled in the rock in titanomorphite. Ptilolite is not present in the cores containing adularia, although the deposition of the zeolite apparently preceded the formation of adularia. It is suggested that the ptilolite, being preferably a soda-lime zeolite, is destroyed during the replacement of soda and lime by potash. The alteration by base exchange was described in great detail by Fenner (6), who states that this process is now active in the Upper Basin in Yellowstone Park.

Banwell [7] measured the temperatures in drill hole 11 between 701 and 895 feet where adularia occurs. The temperature varies from 198° to 213° C and may be compared with the results of mineral synthesis obtained by Gruner (8), who synthesized adularia at temperatures between 245° and 300° C in an alkaline environment. His results reveal that at a lower temperature, a longer time is required for the synthesis of adularia. This fact seems to explain the comparatively low temperatures prevailing at Wairakei, if it is agreed that geological time is also an important factor in hydrothermal alteration.

Hydrothermal solutions that leave the zone in which adularia forms, are enriched in soda and lime; both these ingredients are, at least partly, deposited at higher levels where ptilolite, mainly a soda-lime zeolite, is formed. Perhaps similar solutions with an excess of soda and lime, as well as silica penetrated in the area of drill holes 5 and 6 and there deposited albite and quartz. This would imply that these solutions are of higher temperature than the solutions depositing ptilolite in the other drill holes.

According to Allen (2) and Fenner (6), the potash content of hydrothermal solutions entering the zone of feldspathization is partly derived from magmatic emanations but mainly by leaching the rocks underlying the zone in which soda and lime in the rock are substituted by potash. Thus, this zone of primary leaching presumably separates the zone of feldspathization from, and extends down to, the interface of the magmatic emanations and the lower limit of the meteoric water shell. The drill holes on D-line have not penetrated into the primary leaching zone.

From the described arrangement of the zones in the meteoric water shell one may conclude that the zone of feldspathization is approximately more than half-way down in the meteoric water shell. The distance of this zone from the interface will, apart from other factors, depend much on the presence or absence of interbedded unreactive argillaceous rocks. The thickness of such

[7] Op. cit., p. 9.

rocks will be an important factor controlling this distance. Fenner (6) estimated that in Yellowstone Park the interface is about 850 feet below the surface and that the temperature at the interface is about 300° C.

CONCLUSIONS.

The present investigation has revealed that:

(1) Tuffaceous and arenaceous rocks that have been altered by hydrothermal reagents, and interbedded argillaceous rocks, which are impervious, remain unaltered.

(2) Hydrothermal alteration at Wairakei is characterized by zoning: four zones of progressive alteration may be distinguished.

(3) The drill holes on D-line have not penetrated into the primary leaching zone, which is presumed to be below the zone of feldspathization and extends down to the interface.

NEW ZEALAND GEOLOGICAL SURVEY,
WELLINGTON, NEW ZEALAND,
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REVIEW OF PHYSICO-CHEMICAL DATA ON THE STATE OF SUPERCRITICAL FLUIDS.

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ABSTRACT.

X-ray diffraction and related data on structure of dense gases and liquids are reviewed. It is concluded that the specific volume is one of the major controls of the properties of fluids, especially solubility of non-volatile compounds. It is also concluded that the liquid state of matter extends without limit above the critical temperature and that water within the earth along the normal geothermobars is in the liquid state.

INTRODUCTION.

RECENTLY, it was proposed that certain terms in current use in theoretical geology should be revised, since new facts cannot be accommodated without doing violence to the old theories (91; 93).[1] In brief, it was proposed that processes of mineral deposition by gases should continue to be grouped under the generic term pneumatolysis, but that when the responsible fluids have densities in the range in which they have properties like liquids rather than gases, the processes should be termed hydrothermal. It was pointed out that discrimination between the two processes could be placed on a factual basis (degree of filling of fluid inclusions) and speculation would be unnecessary.

It was expected that some opposition would be expressed by practicing economic geologists, but so far it has been by geophysical chemists (67; 47), and principally over whether the liquid state can exist above its critical temperature. That it can so exist, was assumed by the writer on the basis of general ideas long before formulated by Hannay (37), and more recently restudied by a number of physical chemists and physicists. These data were not quoted in the arguments raised against the concept, and they might have escaped the notice of some of the theoretical geologists who deal with such matters. Therefore, an effort was made to collect all the pertinent physico-chemical facts on liquids, gases, and fluids, under, at, and above the critical temperature, paying particular attention to data on water and carbon dioxide in the ranges of 0–1,000° C and 0–6,000 bars.

Knowledge of the properties of fluids (both liquids and gases) in the above ranges of temperature and pressure within the earth is essential to the understanding of processes of pneumatolytic and hydrothermal mineral deposition, pegmatite formation, and even magmatic differentiation. At present there are serious divisions of opinion regarding silicate–water fluid miscibility relations, and the gaseous or liquid character of aqueous magmatic derivatives (36; 34; 35; 102; 25; 26; 90; 45; 71; 67). This is not a simple problem to

[1] The numbers in parentheses refer to bibliography at end of paper.

state in terms familiar to geologists, but since the physicochemical relations are frequently discussed by geologists, and not always correctly, it is necessary to examine the fundamental facts involved.

REVIEW OF THE PHYSICO-CHEMICAL DATA.

Gaseous State.

The earliest equations of state of gases were based on assumptions of continuous or non-atomic conditions of the gas. Later equations allowed for the size of the constituent particles, the decrease in entropy resulting from decrease of volume, increase of order, and so on. Modern exact equations of state are very complex, but it appears that there is still no general equation that fits all gases at high density. Their properties are specific and not readily predicted, and the methods of treatment resemble those applied to liquids.

There is general agreement among physical chemists as to the meaning of the gaseous state. The usual picture is of atoms, ions, or molecules having freedom of motion over distances very large compared with their own size, and being in the field of their neighbors for an insignificant part of the time, that is during momentary impact.

Structure of Dense Gases.

When the density of a gas is increased, a point is reached when the average free path of the constituent particles is so small that each is in the field of its neighbors for an appreciable part of the time. Mayer and associates calculated the effects of clustering when this point is reached, and were successful in explaining many of the experimental results of Maass and others. A descriptive treatment of the theory was given by Harrison and Mayer (39). According to this general theory, which is supported by a large body of data, the close approach of the constituent particles allows formation of the dense (liquid-like) state by pairs, then triplets, and so on, until the clusters are of microscopic size. The effect leads to peculiar types of phase changes slightly above the maximum temperature at which a meniscus occurs in one-component systems.

The size of liquid-like clusters in gases has been measured indirectly by various thermal diffusion methods (30; 84). The results show an increase in average number of molecules per cluster with decrease of temperature and increase of density.

The degree of clustering of molecules in dense gases can be calculated from P-V-T data. MacCormack and Schneider (59), assuming clustering of CO_2 into pairs, calculated the percent of the paired molecules, from 0–200° C and 1–50 Atm. The apparent clustering of CO_2 decreases with temperature and increases with pressure, rising in value rapidly as the critical point is approached. Dorsey (21) reviewed the data on clustering (association) of water molecules in the vapor and gas states, and concluded that at low densities, water vapor consists of single H_2O molecules, but is associated into temporary clusters of two molecules when the specific volume is less than about 30 cm^3/gm.

The strongest evidence of clustering in dense gases is the X-ray diffraction at low angles. Gases give a scattering of X-rays that is greatest near, or at, zero angle from the beam, falling off rapidly with angular departure. With increasing density, the maximum of scattering does not move out from the zero angle position, but a peak begins to rise at some angle characteristic of the liquid state of the substance. With continued increase in density the curve of scattering due to gas decreases sympathetically as the peak curve (or curves) rise(s) until there is almost no low angle scattering. At densities greater than at this point, the X-ray diffraction is sensibly the same as that of the liquid state, with at least one well defined peak, and generally several peaks resembling diffraction patterns of very small crystals. This is discussed below in more detail with relation to the structure of liquids.

Vineyard (103) calculated the size of the liquid-like clusters in gaseous argon near the critical point, from X-ray data. The clusters must be very small, containing an average of only 9 atoms. Wild (107) used an X-ray diffraction method to measure the dynamic clustering to a high density (liquid-like) state which takes place in nitrogen vapor and gas. The average size of the clusters increased with pressure in the supercritical region.

It is important to note that the data and calculations lead to a picture of a dense gas as being composed of temporary clusters of particles bonded together, dynamically at equilibrium with separate particles having a gas-like distribution (55). The alternative picture of the distance of separation decreasing with density, with momentary inter-action only during impact, is not probable.

Gaseous Solutions.

It is considered by most physical chemists, who have dealt with the matter, that *ideal gases* cannot have solvent properties in the same sense as liquids, because gases have a negligible amount of interaction between their components. Gases and/or vapors may mix over all proportions, and such mixtures have nearly perfect disorder (large entropy). However, just as there is departure from the simpler types of P-V-T laws of gases approaching high density conditions, *real* gases have some specific solvent properties, which increase in importance with decrease of volume, and these solvent properties qualitatively resemble those of the corresponding liquid state (43).

In other ways mixtures of dense gases have been found to resemble liquid solutions. Basset and Dodé (7) found that the solubility of N_2 in H_2O increases with pressure up to a maximum and then decreases. Kritchevsky (52) calculated that the maximum solubility should occur in this type of system when the mole volumes of the gaseous component become equal in the two phases. Kritchevsky (53) and with Tsiklis (54) found a region of immiscibility in mixtures of N_2 and NH_3 above the critical temperature of the system, but at very high pressure. Bridgman (13), commenting on these results, stated that it may be misleading to consider such dense systems as gaseous, even though one or more of the phases are gaseous by classical definition. Robin and others (86; 85) studied the solubility of organic compounds in compressed phases (N_2, A, H_2) and found that the solubility in-

creases with both density and temperature of the gas. Similar conclusions were reached in a number of studies of solubility of inorganic compounds in superheated steam; these will be discussed below.

A number of investigations (recently reviewed by Booth and Bidwell (11)) have demonstrated that when a liquid solution of a non-volatile compound is heated in contact with its vapor in a closed container, the solute remains in solution in the fluid above the critical temperature, unless the volume is allowed to increase substantially greater than the critical volume. These experiments were often interpreted to mean that the liquid state persists above the critical temperature.

Liquid State.

A cursory survey of chemical textbooks shows that definitions of the liquid state have become progressively less specific as knowledge of the state has increased. At one time the definitions included: 1) lack of strength, 2) possession of surface tension, 3) ability to reach equilibrium with its vapor.

It is obvious that liquids of low viscosity have no strength in that they flow without rupture when deformationally stressed. On the other hand, glasses far below the softening temperature may have very high or infinite viscosity, measurable elastic limits before rupture, and other strength properties of crystalline solids. Between these two extremes of viscosity, liquids may be considered to have strength toward stresses applied and relaxed sufficiently rapidly, but no strength toward stresses acting sufficiently slowly. Therefore the zero strength criterion of liquids has general validity only if stresses are applied infinitely slowly, which presents obvious experimental difficulties. Also, under these conditions, some crystalline solids, especially polycrystalline metals, lack strength because of internal diffusion, intergrain diffusion, and so on. Of course, the strength criterion is not useful in the present discussion, because the states of gas and liquid are being compared.

Liquids have a surface tension, or force of coherence which, if satisfied, would keep every body of liquid spherical. The real expression of this force is possible only when a free surface of another immiscible body of no strength is in contact, *i.e.*, a gas, vapor, or liquid. If the pressure on a pure liquid is greater than its vapor pressure, then surface tension is an abstract concept.

The criterion that a liquid may reach equilibrium with its vapor likewise disappears at pressures above the vapor pressure curve. It is obvious that the liquid state does not occur only along the vapor pressure curve, although it is common to so define the extent of the state of vapor (33, p. 244). It is also obvious that the property of having a free surface is not general, because a pure liquid under a pressure greater than its vapor pressure may still be in the liquid state, but no free surface exists, and in fact no surface will appear over a large range of variation of both pressure and temperature simultaneously. Morey (67) defined the liquid state in the following manner. "A liquid is a non-crytalline phase which does not tend indefinitely to expand and fill the available space; . . ." This definition is not applicable, since an expansion of a fluid (suspected of being in the liquid state) changes its proper-

ties. One can take a liquid and allow it to expand indefinitely without a discontinuity, provided the T and P conditions go around the critical point, as has been known from the middle of last century. In other words, the definition should refer to the fluid *as it is,* and not to what would happen if the pressure or the temperature were changed to some other values.

Several authoritative physicochemical textbooks were consulted, but no rigorous definition of the liquid state was found. If the conditions of observation are such that a free surface of liquid occurs, it is not difficult to define the state, but there appears to be no simple criterion in general use for the high pressure conditions of interest to geologists. However, X-ray diffraction results have indicated that criteria based on structure of the state may be valid at any pressure. This will be discussed below.

Structure of Liquids.

The modern picture of the liquid state is due to the work of a number of investigators, principally Lennard-Jones, Devonshire, Bernal, Fowler, Hildebrand, Stewart, Frenkel, Maass, and Gingrich. There appears to be an overall general agreement on the structure of liquids and also some progress has been made in deducing the chemical properties of liquids from their structure.

The relation of liquids to gases and solids was discussed by Lennard-Jones (56), Frenkel (23), Gingrich (32), and Glasstone (33, pp. 510–514). They, and other authorities in this field, appear to consider the liquid state more in the nature of a disordered crystalline solid, rather than of a dense gas. The short range order (coordination) of the crystalline state may be retained, but the long range order (lattice) is nearly lacking in the liquid state. The constituent particles of liquids are in nearly constant interaction with their neighbors, as in crystals, but there is no permanency of position and identity of next nearest neighbors.

The structure of liquids has been considered to be a compromise between:

1) close-packing arrangement of the constituents, wherein any one particle is surrounded by 12 particles (74; 57; 41),

2) regular coordination of next nearest neighboring particles, in other than close-packed arrangement, such as 8, 6, 4, or 2 (9; 82; 73; 79; 80; 104; 105),

3) close-packing or other simple arrangement of the regularly coordinated groups of particles (9),

4) mutual orientation of neighboring regular arrangements to form a regular cluster (cybotactic group) resembling crystal structure (96; 76; 97; 8; 94; 75; 78),

5) mutual orientation of cybotactic groups into liquid crystal units (97; 100),

6) thermal disruption of liquid crystal units, cybotactic groups, coordinated groups, and even bonded pairs to form a random, gas-like distribution of particles, with consequent holes in the structure (76; 27; 56; 22; 23; 5; 83; 88).

The volume of liquids is greater than that of the corresponding crystal(s), neglecting a very few anomalies, and this has been explained as following from the disorder which develops during melting. Even though the average interatomic distance of bonded atoms may remain the same during melting, the volume increases because a disordered group cannot be packed as densely as can an ordered arrangement. Holes occur in liquids wherever cybotactic groups are not aligned perfectly (analogous to dislocations in crystals, but of greater number). In addition, larger holes of thermal equilibrium have been postulated in liquids, these decreasing in relative volume as the density increases (*27*; 23; 15). Bridgman (15) showed that after the holes in liquids are closed up by increase of pressure, the compressibility is nearly the same as that of the corresponding solid.

The structure of liquids, during change of temperature and pressure, may show discontinuities, which have been compared to structural transformations of crystals. Gingrich (3) found a discontinuity in the viscosity of liquid sulphur near 160° C, due to an abrupt change in the structure, especially the average interatomic distance. Antonoff *et al.* (2; 3; 4) and Zlavyansky (108) found multiple discontinuities in water and other liquids by plotting accurate property data against temperature. The discontinuities are small and of second order, but real.

The X-ray scattering from liquids is not as well-defined as from crystals, but consists of similar periodic spectra, which can be analysed very much like diffraction spectra from powdered crystals. The resolution of the diffraction lines of liquids is generally only great enough for measurement within a glancing angle of 10° from the beam, and sometimes only one, but up to about five lines have been measured. The poorly defined X-ray diffraction lines of liquids resemble those of finely powdered or colloidal crystals, and Stewart (97) illustrated a case where the diffraction patterns of a finely-ground crystalline compound and of the same compound in the liquid state, are the same as far as spacing and relative peak height of lines are concerned, but the peaks are not as well defined (*i.e.*, each constituent curve is broader).

The X-ray diffraction patterns of glasses resemble those of liquids. Warren (106) analysed the diffraction by silica glass, and found the Si-O distance to be the same as in crystalline forms of SiO_2. Morgan and Warren (73) pointed out that the X-ray diffraction patterns of glasses and liquids show some differences, especially the first line (smallest scattering angle), which is fully resolved for glasses, and only partly resolved for liquids.

The X-ray diffraction patterns of liquids have been found to change with density. At the melting point, very little small-angle scattering characteristic of gas distribution appears in the curve of scattering, but when the temperature is increased (keeping the pressure equal to the vapor pressure of the liquid) the pattern characteristic of the liquid state decreases in intensity sympathetically as the small angle scattering curve of the gaseous state increases in intensity. At the critical point, both types of diffraction are recorded. When the temperature is increased with the pressure kept constant, and slightly above the critical value, the pattern due to the liquid state dis-

appears at some temperature slightly above the critical temperature (76; 22). When the heating from temperatures near the melting point is carried out under constant volume conditions, there is little or no change in the ratio of intensity of gas-like and liquid-like diffraction, even far above the critical temperature (76; 97; 8; 94). Campbell and Hildebrand (16) found by X-ray diffraction analysis that the structure of liquid zenon is sensitive to its specific volume. At different temperatures the structure remains nearly the same if the pressure is varied to keep the volume constant.

Bernal and Fowler (9) developed a consistent and generally accepted theory of structure of water and aqueous solutions. The unit of structure is an irregular tetrahedral coordination of each HOH group, arranged in three kinds of continuous networks:

1) tridymite-like below 4° C,
2) quartz-like between 4° and approximately 200° C, and
3) ammonia-like (close-packed), from 200 to 340° C.

The arrangements are not perfect and are gradational. Solute ions are accommodated by development of specific ion-water groups with coordination numbers very nearly the same as in crystals. Ionization of water consists of breaking of H-O links such that there can be said to be OH_3^+ and OH^- groups (a fictitious concept, because the continuous network prohibits such ions except momentarily). The hydrogen ion then migrates by energy exchange with neighboring groups such that the same hydrogen ion does not move, although the ionic condition does move; the bodily movement of OH_3^+ ions cannot account for the measured rapid rate of movement of virtual H^+ ions. Randall (82) gave a very similar picture of the structure of water. Morgan and Warren (73) confirmed the partial tetrahedral coordination of H_2O molecules up to at least 83°, by X-ray methods. The two principal concepts of liquid water structure (dissociation-association and quasi-crystallinity) were reconciled by Gierer and Wirtz (29). They ascribed the thermal anomalies of water to the average dissociation of hydrogen bonds, and the volume anomalies to different types of coordination. Pople (79; 80) discussed the influence of electronic orbits in molecules on the properties of aggregations of molecules, specifically in the case of water. In the equivalent position, the electronic structure of a water molecule (H_2O) is described by two sets of two equivalent orbitals pointing in nearly tetrahedral directions, these being the directions of greatest spacial repulsion. The transfer of electrons from hydrogen to oxygen is of small order. Wang (104; 105) studied the structure of water by rate of self-diffusion of hydrogen and oxygen isotopes. He confirmed the continuous semi-crystalline structure up to 55°.

Several investigators have pointed out that the structure of a liquid is of first importance in determining its properties as a solvent. Hildebrand (40) derived a method for calculating the structural entropy of liquids. In discussing effects of liquid structure on solvent properties, he mentioned the probable effect of solutes on the structure of solvents. Stewart (98) found changes in the structure of water (by X-ray diffraction methods) with con-

centration of ionic salts in solution, and these changes can be related directly to the density and apparent molar volumes of salts in solution.

The structural relations between liquids and crystals at the melting point are not directly pertinent, but the data reviewed show that the structure of the liquid controls nucleation of stable or metastable phases (15, p. 243), and there are viscosity and density changes in liquids as the freezing point is approached within a few degrees (87). Oriani (78) calculated the entropy of disordering during melting of metals by subtracting the calculated volume change effect from the total measured entropy change. The results indicated a relatively small percentage of disordering during melting, from 9 to 15 percent in the case of 12 metals considered. Therefore, approximately one atom in every ten along any line through the liquid is not in an ordered position in a cybotactic group, and each cybotactic group contains roughly 1,000 ordered atoms at the melting point.

Critical Phenomena.

Critical phenomena of pure liquids received a considerable amount of study soon after discovery about the middle of last century, and this has been renewed (with emphasis on structure and thermodynamics of the phases) in the last twenty years. Most of the earlier results, and a small amount of the later, are incorporated in current geological hypotheses. Because the more recent data are incompletely discussed in geological works, there has been a tendency for clashing of extreme viewpoints in geological polemics. It is not one of the purposes of this review to discuss all of the theories relating to the critical point of liquids, because it will be demonstrated that normal geothermobaric curves will not pass through the critical point of fluid solutions within the earth. There are several excellent modern reviews of the data and problems, notably by Schröer (89), Tapp, Steacie, and Maass (101), Stewart (97), Spangler (94), Harand (38), Barnes (6), Clark (18), Harrison and Mayer (39), Maass (58), McIntosh and Maass (61), Eisenstein and Gingrich (22), Rice (83), and Atack and Schneider (5).

The critical temperature of a system may be defined as the temperature below which it may exist in two phases in stable equilibrium (liquid and gaseous), and above which these two phases are not stable together. The old concept that only gas can exist above the critical temperature is no longer tenable (17). Expressed in other words, the liquid state, in which most of the constituent particles are bonded, and grouped into various types of order to various degrees, is a function of temperature and volume, with no discontinuity at the critical temperature and/or critical pressure. Similarly, the gaseous state, in which most of the constituent atoms, molecules or ions are not bonded to their neighbors, but in which the clustering into liquid-like groups is a function of temperature and volume, has no discontinuity at the critical temperature and/or critical pressure. Consequently, the distinction between the states of liquid and gas depends upon arbitrary limits of certain kinds of measurements (density, percentage of bonding, continuity of bonding network, size of cybotactic groups, etc.). In a certain special range of conditions,

that is, along the vapor pressure curve, the distinction is not arbitrary, because the two phases are immiscible. From data of X-ray diffraction, diffusion, solubility, reaction rates, density, compressibility, and sound absorption, distinction between the states of liquid and gas becomes less definite and mixtures of the two extend over a larger range of temperature at any pressure, and of pressure at any temperature, the higher the temperature and pressure are above the critical values. This must be due primarily to the volume effect, because the isometric curves in the T–P plot converge toward the critical region Very approximately, the median between the liquid-like and gas-like condition in the supercritical region is along the critical volume curve.

Mayer and Streeter (60) discussed various types of first and second order phase transitions (simple first order, anomalous first order, diffuse first order, "lambda," and simple second order). They showed that experimental data support the concept that the liquid–gas phase transition, in the critical region, is of anomalous first order type. The liquid phase becomes broken up by inclusion of the gaseous phase, and the latter develops clusters of liquid phase, when the critical point is approached from either side. They showed that the transition point in a liquid–gas phase change is that point where the compressibility reaches a maximum. This criterion can be used: 1) far below the critical temperature, where the transition is of simple first order type, 2) at the critical temperature, where it is of anomalous first order type, and 3) far above the critical temperature, where it is of the diffuse first order type. This criterion is useful if it is desirable to place an exact limit between the ranges of conditions in which supercritical fluids have properties of liquids and gases. However, it will be evident that the sharpness of the transition, and therefore the usefulness of the gas–liquid limit, both become less the farther the temperature and pressure are above the critical values. The anomalous (and diffuse) transition appears also as a maximum in the specific heat of carbon dioxide at the critical density, extending at least 100° above the critical temperature (63), and also as a minimum in the velocity of sound in carbon dioxide at the critical density, extending above the critical temperature (1).

X-ray diffraction data indicate that there is a difference between the liquid and gaseous (also vaporous) states, and that the fluid at the critical point appears to be a mixture of two states. Therefore, it seems permissible to consider the two states to have limited mutual solubility below the critical temperature, and unlimited mutual solubility above the critical temperature, very much like partly immiscible liquid pairs.

It is interesting that stable emulsions of liquid and gas (vapor) may be formed even in pure one-component systems, very close to the critical point. This appears as a milky opalescence which has been reported and studied by many investigators. Atack and Schneider (5) studied the properties of this type of emulsion by a radioactive tracer technique. The stability of discrete liquid clusters in ethane, big enough to sink in the gas, and also large enough to scatter light, was demonstrated to extend about 0.3° C above the critical temperature (temperature of disappearance of meniscus) when the system had the critical specific volume. Blosser and Drickamer (10) measured the

scattering of monochromatic light by methane and propane in the critical region. They found that the degree of scattering (which indicates the degree of heterogeneity of the fluid) in both cases increases with temperature approaching the critical temperature, reaches a maximum slightly above it, but decreases again above the critical temperature. That is, there is inappreciable heterogeneity in both the liquid and gaseous states, but there is considerable heterogeneity when one state changes to the other, even when no gross phase boundary can occur. Meissner (62) observed heterogeneity in CO_2 below and above the critical temperature using a dark-field microscopic technique.

Solutes with a low vapor pressure are much more soluble in the liquid state of a solvent than in its vapor, but the partition coefficient approaches unity nearing the critical point. Although the partition coefficient moves from high values toward unity, the solubility itself may vary in an irregular way, determined by the solute, solvent, and the temperature. For example, the solubility of NaCl in liquid water increases with temperature along the vapor pressure curve of the solution, but the solubility of Na_2SO_4 in liquid water first increases slightly, then decreases very greatly under the same conditions.

Solutes with a high vapor pressure (usually considered as gaseous components) mix more readily in the vapor state of a solvent than they dissolve in the corresponding liquid state, but the partition coefficient becomes unity at the critical point. Below the critical temperature, the partition coefficient of the gaseous solute is not independent of pressure, because at very high pressure a limit of solubility in the liquid phase can be realized (7; 53; 54). From considerations of the structure of the phases involved, it would appear that the solubility of a more volatile component (A) in a less volatile component (B), when a liquid phase (B, A) and gaseous phase (A, B) are in equilibrium, must be an exceedingly complex relation. Among the processes involved, the available data suggest the following:

1) mixing a A in the random or gas-like distribution within the liquid;
2) solution of A in the cybotactic groups in the liquid;
3) equilibrium between order and disorder in the liquid, dependent on T, V, and ratio of A to B;
4) mixing of B in the random or gas-like distribution within the gas;
5) solution of B in cybotactic groups (or clusters) in the gas;
6) equilibrium between order and disorder in the gas, dependent on T, V, and ratio of A to B.

Superimposed on these dynamic equilibria are possible structural changes of the two kinds of cybotactic groups, and of the degree of order within such groups, both of which will be more important in the liquid phase.

In many ways, the mutual solubility of two liquids is analogous to that of a liquid and its vapor (43), and the multiple equilibria suggested above appear to be applicable. Partly miscible liquid pairs have mutual solubility curves which unite at a critical solution temperature, and the shape of the full miscibility curve resembles qualitatively the full curve of density of liquid and vapor

against temperature. In the case of liquid-liquid immiscibility, pressure has an effect on the miscibility and on the critical solution temperature. In general, increase of temperature at constant volume increases the mutual solubility of two partly-miscible liquids, while decrease of volume at constant temperature decreases the mutual solubility.

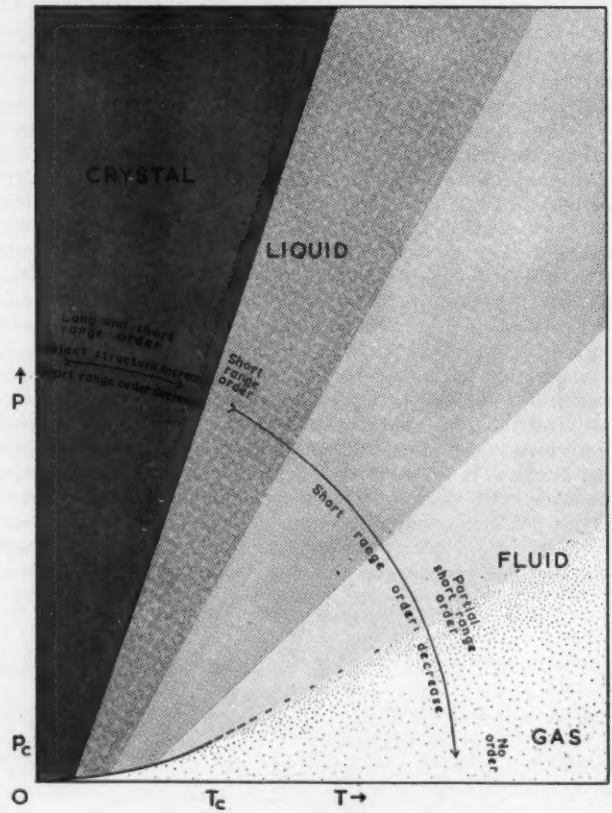

FIG. 1. Schematic one-component phase diagram showing the crystal–liquid equilibrium extending to higher temperatures than the critical point of the liquid–gas equilibrium.

Phase diagrams of one-component systems usually are not illustrated in chemical text-books as extending beyond the respective critical temperatures, but it is well known that the melting curve of a crystalline solid will extend indefinitely above the critical temperature (23, pp. 95–96; 14, pp. 207–208).

This is shown schematically in Figure 1. Apparently there are no data on the structures of fluids in equilibrium with crystals at super-critical melting temperatures, but nothing was found in the literature to suggest that they are qualitatively different from the structures of liquids at sub-critical melting temperatures. For example, the melting curves of He, CO_2 and a number of other compounds have been determined above the respective critical temperatures, but no discontinuities at the critical temperatures are recorded (44; 14, p. 207). Unless some novel factor disturbs the quasi-crystalline or cybotactic structure of liquids it is to be expected that this should persist along the melting-freezing curve to very high temperatures (with the probability of changes of structure along this curve due to decrease of volume at the very great pressures involved). In other words, any stable crystalline solid probably melts to a liquid, at any temperature above its triple point, and the critical temperature of liquid–vapor equilibrium does not influence the liquid–crystal equilibrium. Consequently, it is probable that the liquid state extends above the critical temperature, and its limits are related more to the melting curve than to the boiling curve, as shown in Figure 1.

One argument that may be raised against the concept of the liquid state persisting above the critical temperature is that only terminology is being considered, and that, by definition, fluids above the critical temperature are gases. However, the same type of argument can be used in rebuttal. That is, definitions of melting involve equilibrium between crystalline solid and liquid, and as indicated above, the melting curve extends above the critical temperature of the liquid–vapor equilibrium. Therefore, by definition, the liquid state extends above the critical temperature. The facts at hand indicate that *both* phases may exist above the critical temperature, but not, of course, in equilibrium with each other.

An attempt was made to make a pictorial summary of the above facts and theories of structure of liquids, relation of liquids to gases, and critical point, specifically for water. The result is Figure 2. This was designed to illustrate, in two dimensions, the following three-dimensional features: 1) imperfect mutual four-fold coordination of each H_2O molecule (filled circles), 2) cybotactic groups in the high-density or liquid state, 3) decrease of density at junctions of cybotactic groups, 4) occasional holes in the liquid larger than molecules, 5) decrease in size of cybotactic groups with increase of temperature, 6) increase of density by decrease in number of large holes with increase of pressure, 7) clustering of molecules in the denser gas, 8) decrease of size of clusters with increase of temperature and decrease of volume, and 9) position of maximum, minimum, and mean geothermobars with relation to the liquid-like and gas-like states of water.

Liquid Solution.

A general discussion of solution of non-volatile compounds in liquids is beyond the scope of this review, but the few experiments using solvents such as water at high temperatures and pressures give considerable diagnostic data.

Stewart (98), Hildebrand (40; 41; 42), and Hildebrand and Scott (43)

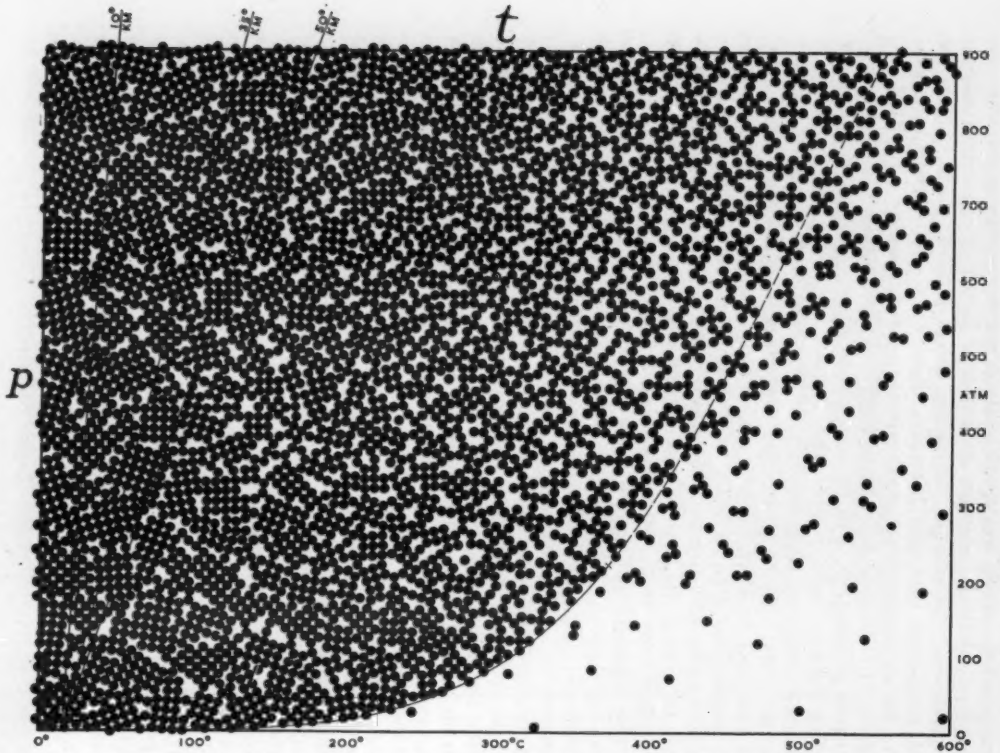

FIG. 2. Two-dimensional representation of the postulated structure of the fluid states of matter in the vicinity of the critical point. The structural and numerical details refer to water.

have shown how complex must be any general treatment of solution in liquids. The implication is that if the internal structure and bonding of a liquid were known sufficiently, one might be able to calculate the solubility of a compound, knowing in addition the new structure and bonding initiated by the solute. However, the present knowledge of the structure of aqueous solutions and other solutions of geological interest is too slight to allow general statements.

Schröer (89), Ingerson (45), Khitarov and Ivanov (49), and Morey and Ingerson (71) discussed the problems of solubility of non-volatile compounds in supercritical fluids. A large body of subsequent work on supercritical solution exists, mostly on organic or other systems which have only imperfect analogies with geological materials. Some of the more important contributions of geological significance are summarized below.

Morey and Ingerson (72) made some measurements of T-P relations in the system Na_2O2SiO_2—H_2O, along the three-phase equilibrium of silicate crystals, hydrous silicate melt and steam, over the ranges 729°–843° C and 200–2,000 pounds per square inch. They reported negligible solubility of sodium silicate in the steam, which was above the critical volume under the experimental conditions.

Kracek, Morey, and Merwin (51) studied the system H_2O—B_2O_3, and among other things, discussed the partition coefficient of the two components in the liquid and gaseous phases when both are at equilibrium with solid phases (0–400° C, 0.1–7 atmospheres). The coefficient is of the order of 300, the gaseous phase having a lower concentration of B_2O_3 than the liquid phase.

Morey (66) discussed the solubility of solids in water vapor, and summarized data on the H_2O—K_2O—SiO_2 and H_2O—Na_2O—SiO_2 systems. He pointed out an essential difference between these systems: in the potassic system, the solubility surfaces of various silicates are continuous, so that the equilibrium between vapor, silicate solution (or melt), and silicate crystals can be followed from low temperature up to the melting temperature of the silicate crystals; in the sodic system, critical phenomena appear, and for a certain interval, only a two-phase equilibrium between vapor and silicate crystals can be realized. At sufficiently high temperatures and pressures, the three-phase equilibrium appears. Morey recorded that the light phase, which he called vapor phase, may contain large amounts of sodium silicate, as much as ". . . over 50 percent by weight of solid material in solution in the vapor."

Straub (99) made an extensive series of measurements of solubility of salts and silica in steam. He found that NaCl, NaOH, and SiO_2 are appreciably soluble, but Na_2SO_4 is not soluble, in superheated steam. The solubility increases with both temperature and pressure. The data concerning the solubility of SiO_2 in steam were found to be internally consistent, giving a series of straight isobars when the log of the solubility in p.p.m. was plotted against the reciprocal of absolute temperature. The ranges of conditions were 400 to 680° F and 67 to 2,710 pounds per square inch.

Klinkenberg (50) discussed the continuity of gaseous mixtures and liquid solutions above the critical point, using the system SiO_2—H_2O as illustration. He pointed out that many of the experiments on volatility of silica in supercritical steam were carried out at pressures under which gaseous water has a

density greater than the critical density. "Therefore the observations might better be described as solubility in water."

Diepen and Scheffer (20) studied the system napthalene–ethylene in a range of temperature and pressure beyond the critical point of the saturated solution. They found concentrations of solute up to 25,000 times greater than those predicted from the vapor pressure of napthalene, and concluded that a specific solubility effect is exercised by the supercritical solvent. They found solubility at constant temperature increases rapidly with pressure; at constant pressure it decreases with temperature at low pressures, but increases with temperature at high pressures.

Friedman (24) measured the solubility of quartz in solutions of NaOH and Na_2CO_3 from 300° to 450° C. The degree of filling of the pressure vessels with the solution was approximately 60 percent. The solubility of quartz was found to increase with concentration of alkali, and with temperature. No discontinuity of solubility at the critical temperature of the solutions (probably about 390°) was found. The solutions at 450° contained a large amount of silica, of the order of 30 to 50 percent by weight, with 15 percent Na_2O as carbonate and hydroxide, respectively.

Tuttle and Friedman (102) and Friedman (26) published data on fluid immiscibility in the system H_2O—Na_2O—SiO_2. Below the critical temperature of water saturated with sodium silicate (about 390° C), and down to 225 ± 25° C, the phases in equilibrium were stated to be silicates (or quartz), silicate liquid, water solution, and water vapor. Above the critical temperature, only one hydrous phase occurs, and the equilibria were studied at various degrees of filling and temperatures. It was found that above the critical temperature, variation of degree of filling did not change the composition of the phases very much, between fillings of 20 and 60 percent. The compositions of the two fluid phases in equilibrium with quartz are reproduced below.

Temp. C	Total composition			Silicate liquid comp.			Hydrous fluid comp.		
	SiO_2	Na_2O	H_2O	SiO_2	Na_2O	H_2O	SiO_2	Na_2O	H_2O
250	33.9	13.0	53.1	45.5	17.5	37.0	21.8	9.0	69.2
300	35.1	12.9	52.0	51.0	18.0	31.0	17.2	6.7	76.1
350	36.1	12.6	51.3	55.4	20.1	24.5	12.1	4.5	83.4
400	22.2	7.4	70.4	59	20	21	7	3	90
400	14.3	4.9	80.8	59	20	21	4	2	94
450	22.6	7.4	70.0	60	16	24	8	3	89
450	15.0	5.0	80.0	61	20	19	5	2	93

It is evident that there is no major discontinuity of solubility of sodium silicate in the hydrous phase on passing through the critical temperature. The considerable solubility of sodium silicate in the supercritical hydrous fluid (6–11%) is noteworthy, also that the Na_2O/SiO_2 ratio in the hydrous phase is greater than in the silicate phase, both below and above the critical temperature.

Friedman (25) made a test of the solubility of potassium silicate in the gas phase in equilibrium with melting $KHSi_2O_5$ at 400° C. Less than 1 percent of non-volatile components was found. The pressure was not given, but from data of Morey and Fenner (68) this would be less than 100 atmospheres.

Booth and Bidwell (11) reviewed the principal published data on solubility in fluids near the critical point. They found fairly general agreement that: 1) solutes become increasingly soluble in saturated vapor approaching the critical temperature, 2) there is no discontinuity of solubility on passing through the critical temperature provided that the volume of the fluid above that temperature is the same as the volume of the liquid below that temperature, 3) solubility increases with temperature above the critical temperature when the volume remains constant, and 4) solubility increases with density of solution above the critical temperature. These conclusions can be further generalized to the concept that compounds soluble in a liquid are also slightly soluble in the corresponding vapor, and above the critical temperature, the solubility is of somewhat similar order to that in the liquid when the fluid is dense, and similar to that in the vapor when the fluid is diffuse. References were made to 129 works, including most of the important geological contributions. A good summary is given of data on the system water–silica.

Booth and Bidwell (12) measured the solubility of six salts (CaF_2, BaF_2, LiF, $SrSO_4$, $CaSO_4$, Na_2SO_4) in water at elevated temperatures by an analytical method. The solubility of $CaSO_4$ and Na_2SO_4 was found to decrease over the entire temperature range investigated. The solubility of LiF was found to increase with temperature when the density of the solution was over 0.36, but to decrease with temperature below this density. No discontinuity in the solubility curves was found at the critical temperature, critical pressure, or critical volume of the solutions. Above the critical temperature, solubility of LiF increases rapidly with increase of density of the solutions.

Ölander and Liander (77) studied the system NaCl—H_2O near the critical point, especially the partition of NaCl between liquid and vapor slightly below the critical temperature. The critical curve of NaCl solutions was found to lie on a continuation of the vapor pressure curve of pure water. The solubility of salt in steam was found to increase rapidly with pressure, and to decrease with temperature, in the critical range.

Kennedy (48) measured the solubility of quartz in water up to 610° C and 1,750 bars. The solubility was found to increase with pressure at all temperatures, but below a pressure of approximately 700 bars an increase of temperature decreases the solubility. No discontinuities in the solubility curves were detected at the critical temperature and critical pressure. In spite of this, and in spite of current physicochemical concepts, he divided the two-phase field into "quartz + liquid" and "quartz + gas" with a boundary at the critical temperature. Kennedy noted the great dependence of solubility of silica in water upon the density of the solution and pointed out the geological significance of this relation.

Morey and Hesselgesser (69) made some measurements of solubility of

silica (quartz and silica glass) in supercritical steam (300 to 500° C) by a dynamic method, and found an increase in solubility with increase of temperature and density of the steam. They discussed the results in terms of volatility, but rejected this explanation. "The amount of silica in the steam is so enormously greater than would be expected from the vapor pressure of quartz that a true solubility in steam is the only possible explanation." Morey and Hesselgesser (70) extended their determinations of solubility of minerals in steam, and results for quartz, feldspars, enstatite, several sulphates, cassiterite, hematite, and sphalerite were reported, in the range 500–600° C. and 1,000–2,000 bars. The data for quartz were shown to be very similar to those rereported by Kennedy (48). They showed that the solubility of quartz in the range of experimental conditions increases with temperature and density of steam. "It is evident that solubility is determined not by pressure but by the amount of water present."

The solubility of non-volatile compounds in supercritical H_2O (often called supercritical steam) can be related directly to the solubility in liquid water. It is evident that, if the solubility at constant pressure increases with temperature below the critical temperature, it has the same effect above the critical temperature, with no evidence discontinuity at that temperature. Similarly, there is no discontinuity of the solubility at constant temperature on passing through the critical pressure.

In the range of conditions where water solutions have specific volumes greater than they would have at room temperature, the effect of decrease in volume is to increase the solubility of silica (and probably also silicates and alkali halides) in the solutions. Taking into account the data discussed above, this effect can be ascribed to the volume dependence of order-disorder in the fluid: at small volumes the number of holes and gas-like parts of the fluid is proportionally smaller than at large volumes.

The effect of temperature on solubility of silica (and probably also silicates, alkali halides, and many other compounds) in water is positive, provided the volume remains constant. This appears to be a general relation in condensed systems. Because of the interrelations of P, V, and T, the relations between solubility, pressure, and temperature are more difficult to state in a simple manner. It is obvious, however, that below some pressure (which is not the critical pressure) increase of temperature at constant pressure decreases the solvent powers, due to the volume increase lowering the solubility more than the temperature increase raising the solubility. Above this pressure, increase of temperature at constant pressure increases the solvent power. This pressure limit of retrograde temperature effect of solubility at constant pressure was found to be approximately 700 atmospheres in the case of silica in water (48).

Fluid Solutions Under Geothermobaric Conditions.

The critical temperatures of liquids which have existence within the earth extend over a considerable range, but the critical pressures are similar and small. The critical temperatures and pressures of several volatile compounds

considered at one time or another by geological theoreticians to be important in earth processes, are listed below.

A recent compilation of data on inclusions in minerals (92) has shown that the liquids from which minerals are crystallized, and/or which are present during crystallization, are: 1) silicate solutions, 2) aqueous solutions of salts, 3) carbon dioxide, 4) petroleum. The last probably can be considered not to act as solvent for the components of the common minerals, except CO_2. Carbon dioxide probably does not function as an important solvent in the earth, but the data are meager. Because it is so abundant and ubiquitous in mineral inclusions, it will be considered below as a possible solvent. Consequently, the relations between the critical temperature, critical pressure, and earth T-P conditions, for silicate solutions, saline aqueous solutions, and carbon dioxide, will be considered.

The critical temperatures of pure silicates must be very high since they must be above the boiling temperatures; even their melting temperatures are above the temperature being considered here. Therefore fluid silicates should

Compound	T_c (C)	P_c (Atm)	V_c (cm³/gm)	Source of data
H_2O	374.15	218.39	3.1	(21, p. 558)
SO_2	157.2	77.7	1.9	(28, p. 248)
H_2S	100.4	88.9	—	(28, p. 248)
HCl	51.4	81.6	2.38	(28, p. 248)
CO_2	31.0	72.8	2.156	(81, p. 59)
SiF_4	− 1.5	50	—	(28, p. 248)
CH_4	− 82.5	45.8	6.17	(28, p. 248)
CO	−139	35	3.215	(28, p. 248)
N_2	−147.1	33.5	3.215	(28, p. 248)

have properties of liquids rather than of gases within the crust of the earth. Needless to say, this is not a novel concept.

The P-V-T relations of water, plotted in the form of isometrics from data by Bridgman (14, p. 180) and Kennedy (46), are shown in Figure 3, together with several geothermobars. The depth-pressure relation was calculated for a rock density of 2.7. The smallest gradient (10°/km) is approximately a mean for the Archean part of the Canadian Shield (95, p. 290), the largest gradient (50°/km) is approximately a mean for the young orogenic belts of the Cordillera, Japan, Borneo (95, pp. 281, 282, 284, 286, 290). The average gradient (35°/km) is approximately a mean for the world (95). It is evident that the geothermobaric curves, even the steepest, which probably do not continue indefinitely at the surface gradient (19), lie in that part of the diagram in which water has solvent properties like a liquid rather than a gas. The major effect of nonvolatile solutes would be to move the isometric curves of pure water to higher temperatures. Consequently, water under normal geothermobaric conditions has a density much greater than the critical density, that is, it is in the liquid state, and no discontinuity of properties is probable along any of the normal geothermal gradients.

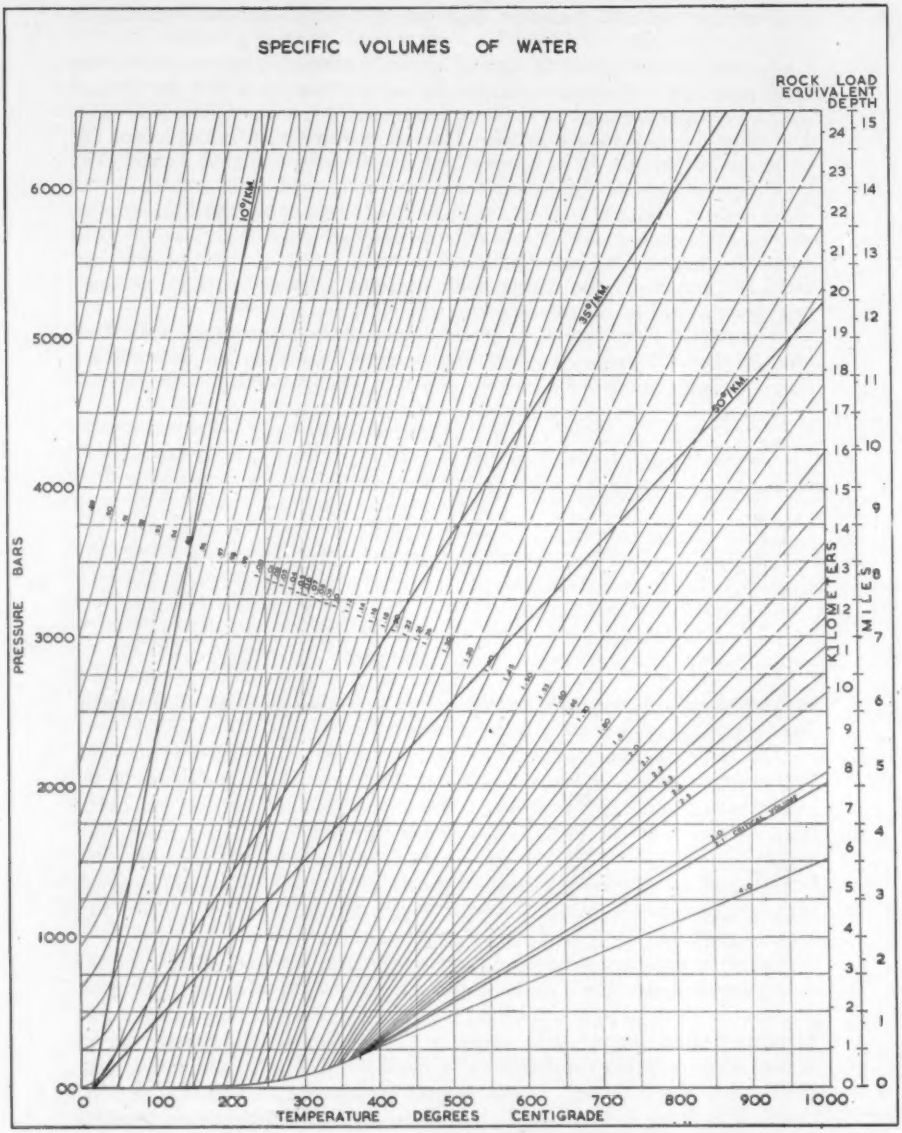

FIG. 3. P-V-T relations of water, with approximate maximum, minimum, and mean geothermobars.

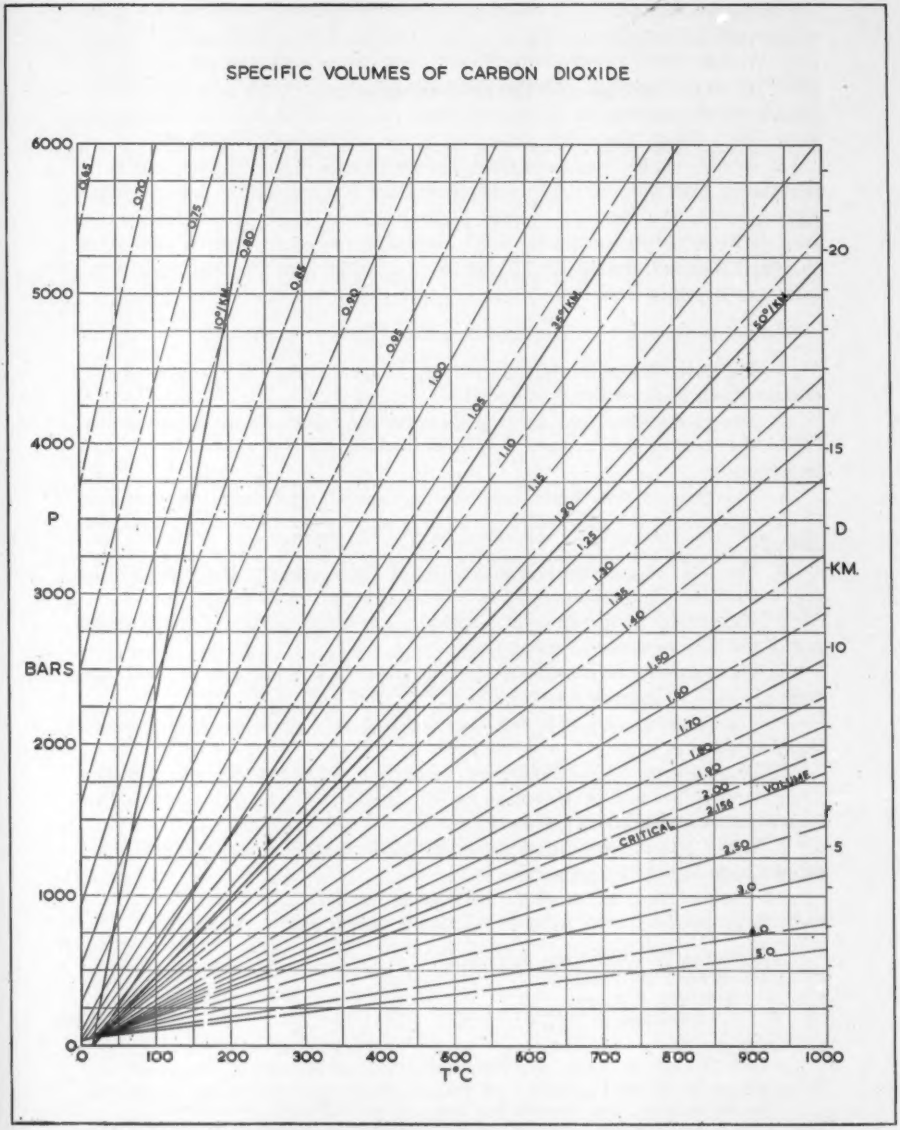

FIG. 4. P-V-T relations of carbon dioxide with approximate maximum, minimum, and mean geothermobars.

The approximate P-V-T relations of carbon dioxide, plotted in the form of isometrics from data by Michels and Michels (64) and Michels, Michels, and Wouters (65), are shown in Figure 4, together with several geothermal gradients as in Figure 3. The geothermobaric curves in this case lie closer to gas-like conditions than in the case of water, but even CO_2 will have properties more like a liquid than a gas along any of the normal geothermobars.

It should not be construed from the above discussion that the writer is postulating that mineral deposition takes place at temperature-pressure conditions within the limits of normal geothermobars. This is another matter entirely from the present thesis, and is dependent on other kinds of facts such as composition and degree of filling of liquid inclusions, and temperature, pressure, and depth of deposition.

CONCLUSIONS.

1. The gaseous and liquid states of matter are distinctly different and give characteristic X-ray diffraction spectra.

2. The gaseous and liquid states of matter have limited mutual miscibility below the critical temperature but unlimited miscibility above the critical temperature.

3. The gaseous and liquid types of aggregation and their mixtures can be detected above the critical temperature and pressure by X-ray diffraction analysis.

4. The ratio of gaseous to liquid types of aggregation in the supercritical region increases with volume and, to a smaller degree, with temperature.

5. The critical temperature and pressure are limits neither of the gaseous nor of the liquid states of aggregation.

6. The solubility of a non-volatile compound in a fluid increases with the ratio of liquid to gaseous aggregation in the fluid.

7. The solubility of a volatile compound in a fluid decreases with ratio of liquid to gaseous aggregation in the fluid.

8. There are no discontinuities of solubility in a fluid at the critical values when temperature and pressure are varied, provided the conditions are above the critical temperature or pressure.

9. Water and aqueous saline solutions under normal geothermobaric conditions have liquid-like properties.

10. Carbon dioxide under normal geothermobaric conditions has intermediate properties, but is more like a liquid than a gas.

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GEOCHEMICAL PROSPECTING FOR COPPER AT RAY, ARIZONA.

OTIS M. CLARKE, JR.

ABSTRACT.

Copper assays of oak and mesquite leaves and the soil derived from them were made from trees growing over the Ray orebody and vicinity. Results show a marked increase of copper in plants and soil over the orebody as compared with samples taken from areas beyond the limits of mineralization. The copper content of trees growing in the stream bed below the orebody was lower than expected. Soil assays are affected by type of rock, drainage and extent of leaching. High erroneous assays are found in regions contaminated by smelter smoke.

INTRODUCTION.

THIS paper is a progress report on experimental work on geochemical prospecting for copper in semi-arid regions. The first objective was to determine whether geochemistry could be used in searching for concealed copper deposits and to learn how these methods might be applied to the greatest advantage.

Most of the work was done in vicinity of the large disseminated copper ore at Ray, Arizona, where the extent of mineralization is fairly well known. Special attention was paid to the surface drainage, with samples taken from both above and below the main orebody. The work consisted of looking for small amounts of copper in dry leaves of plants, and in soil derived from the leaves. Lately, soil surveys have served as partial guides in diamond drilling.

Chemical Procedure.—After some experimenting, the following method of analysis gave satisfactory results: 200 grams of dry leaves were weighed and burned to ash. After weighing the ash, it was digested with nitric, hydrochloric and sulfuric acids. Enough potassium chlorate and sulfuric acid were added to oxidize all organic matter and the samples were boiled until nearly dry. Water was added and they were boiled and filtered. The copper was precipitated from the filtrate with aluminum and determined by the standard iodide method. Iron analyses were made from the filtrate by the potassium permanganate method.

For the soil analysis, 200 grams of soil were leached with 400 cc of 10 percent sulfuric acid solution for a period of about twenty-four hours. Two hundred cc of solution were drawn off and the copper precipitated with aluminum and determined by the standard potassium iodide method.

Geology.—The earliest rocks of the district are the complex Pinal schist, which consists of Precambrian metamorphosed igneous and sedimentary rocks. Quartzites, shales and limestones were deposited in late Precambrian. More

limestone was deposited in the Devonian and Carboniferous periods. Igneous rocks, consisting of diabase, diorite, and quartz monzonite porphyry, intruded the schist and sediments. The mineralization followed the porphyry.

In the period of erosion after the primary ore deposition, the Whitetail conglomerate accumulated in the valleys and lowlands. This and other exposed rocks were covered by volcanic tuff and dacite lava flows in the Tertiary period. The Gila conglomerate was deposited by streams following the eruption.

The conglomerates and dacite have been eroded from the orebody at Ray. They still cover large areas in this part of the state. It is probable that they conceal other orebodies.

The primary mineralization, or protore, consists of innumerable crisscrossing veinlets of pyrite and quartz, with chalcopyrite occurring in zones. These veinlets cut the Pinal schist, diabase and porphyry. Ore occurs where

TABLE I

ANALYSIS OF OAK LEAVES AND SOIL

Rock formation and sample location	% Cu, ash	Ppm cu. in. leaves	Ppm cu. in. soil	Ppm Fe in leaves
Mineralized diabase, Amanda Gulch	0.975	1200	14,200	2300
Schist capping, edge of orebody	0.083	100	149	2480
Schist capping on Bishop Fault—Copper Canyon	0.119	167	550	2740
Schist—Mineralized zone west of orebody	0.037	41	96	1380
Granite—Unmineralized, southwest of orebody	0.015	30	68	2850
Dacite lava, Oak Flats	0.414	500	286	2680
Dacite—Oak Flats	0.337	371	286	2920
2nd sample				
Dacite—South Rim, Devil's Canyon	0.273	437	102	3360
Granite Near Castle Dome—Low shrubs	0.156	125	66	1060
Granite near Castle Dome—Larger tree	0.159	126	66	1400

the upper part of the deposit has been leached, with most of the copper migrating downward to replace the pyrite with chalcocite.

Analysis of Oak Leaves.—It has been noted that oak trees and shrubs grow on the copper deposits at Ray and Miami at a lower elevation than is usually found elsewhere. They grow abundantly on the north slopes, where there is some slight protection from the sun. Although oaks are rarely found below four thousand feet elevation in this climate, they thrive on the mineralized capping growing at an elevation from 2,000 feet to about 2,500 feet. Scrub oak, *Quercus turbinella* and larger trees, emery or blackjack oak, *Quercus emoryi* are found. Since it is possible to use the oak as an indicator plant in searching for other copper deposits, it was decided to investigate the copper content of its leaves and the soil derived from them (Table I).

By burning the leaves and analyzing the ash, it was found that oaks do absorb copper more or less in proportion to the amount of copper available.

The highest assay came from a tree growing on an outcrop of mineralized diabase containing chrysocolla and tenorite (cupric oxide). The leaves contained 0.120 percent copper or 1,200 parts per million with the ash assaying 0.975 percent. Leaves from trees growing on the leached capping of the Ray orebody contained 100 to 167 parts per million, and an oak growing on unmineralized granite southwest of the orebody gave the low assay of 30 parts per million. The iron assays were erratic and they had no relation to the copper content.

Samples were taken from leaves of the low bush shrub and from the larger trees growing in the same location near Castle Dome Mine. The copper content was the same in both species.

Dacite Mystery.—In attempting to find the normal copper content of oaks growing away from copper orebodies, leaf and soil samples were taken from trees growing on top of the thick dacite lava at Oak Flats Recreation Area, near Superior. It was quite surprising to find more copper in these leaves

TABLE 2

ANALYSIS OF MESQUITE LEAVES AND SOIL

Rock formation and sample location	% Cu, ash	Ppm cu. in. leaves	Ppm cu. in. soil	Ppm Fe in leaves
Schist—Mineralized zone west of orebody	0.078	113	96	3880
Granite—Unmineralized, southwest of orebody	0.038	38	54	865
Silt, stream gravel below copper outcrop, Amanda Gulch	0.215	390	420	1060
Silt, gravel. Mineral Ck., edge of orebody	0.055	76	48	1205
Silt, Mineral Ck. 3½ miles south of Ray	0.062	51	56	1290
Silt and gravel. Wash east of Mineral Ck. 3½ miles south of Ray	0.085	57	68	1160
Dacite—North of Ray	0.047	60	50	1570

than in the trees growing over the Ray orebody. To ascertain that there was no contamination of samples, additional samples were obtained and analyzed. The results of the second samples confirmed the high results.

The high copper assays were probably due to contamination from smelter fumes of the Magma smelter at Superior. Although the quantity of copper transported by the smoke would be small, it does not take much to show up as a few hundred parts per million. It has been reported from Utah and Michigan [1] that plants do absorb copper from smelter fumes.

The possibility of the dacite itself being the source of copper was investigated. Analysis was made of mesquite leaves from a tree growing on the same lava flow about a mile north of Ray, where there would be no smoke contamination. Both leaf and soil samples contained very little copper, so it is believed that the dacite was not the source of the abnormally high assays. Copper de-

[1] Utah—Ordonnez, Georges, Oral Communication. Michigan—Brant, A. A., Talk at A.I.M.E. meeting in Jerome, Arizona, May 14, 1948.

posits could occur below the dacite at Oak Flats, but the solutions from them would have to pass up through about a thousand feet of lava flows.

Mesquite Leaves.—In investigating the more common plants of the lower Sonoran Zone of the desert, it was found that mesquite, *Prosopis Juliflora,* absorbs copper similar to the oaks. Since this tree grows in most of the south-

TABLE 3

COMPARISON OF MESQUITE SOILS AND ADJACENT SILTS

Sample and location	Ppm Cu, mesquite soil	Ppm Cu, silt
Schist capping above Ray orebody	576	400
Mineral Ck. north of Ray	169	36
Dry wash one mile south of Ray	30	Nil
Dry wash 2½ miles south of Ray	36	8
Dacite lava north of Ray	50	Trace

western deserts, it was selected for further study. Another advantage is that its roots grow quite deep, and this gives it a better chance to tap water from mineral deposits. Oak and mesquite growing together were sampled in two localities and it was found that the mesquite had the slightly higher copper content of the two (Table II).

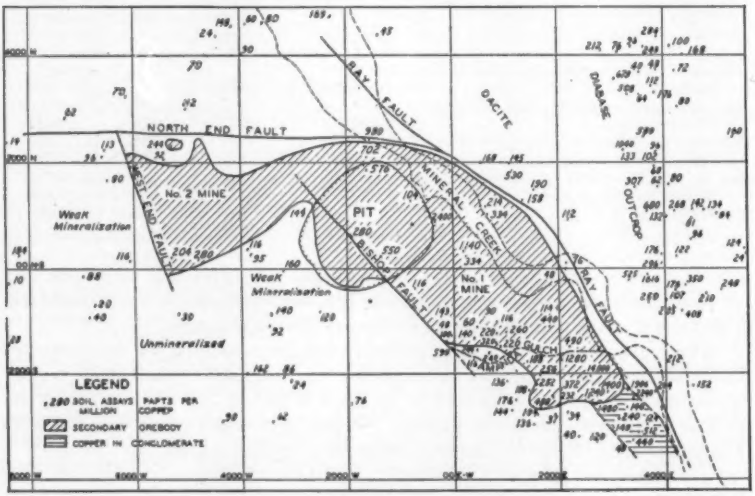

FIG. 1.

Soil Samples.—Soil samples taken below oak and mesquite trees contain more copper than soils and silts from the same location, but away from the trees. The samples were taken to a depth of about four inches and consisted of humus and some of the subsoil. Undecayed leaves and gravel larger than

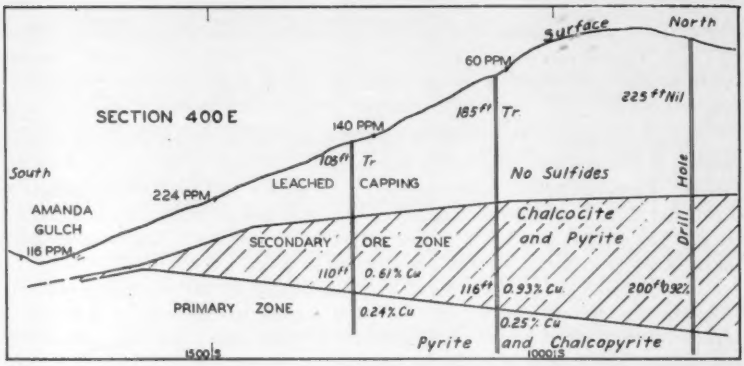

FIG. 2.

sixty mesh were screened out and discarded. Soil samples are easier to obtain, less bulky and much easier to assay than samples of the leaves. The soil has about the same amount of copper as the leaves from which it was derived. Soil under palo verde trees were also used satisfactorily.

RESULTS.

Capping over the Main Orebody.—Soil samples were taken at scattered intervals on the capping over the main orebody, over marginal mineralized areas and beyond the limits of mineralization. The higher assays occurred over the ore and intermediate assays over marginal mineralized areas containing pyrite with almost no copper. Low assays were found beyond the limits of mineralization. There were some erratic results, but most of the orebody could be outlined on the basis of soil samples (Fig. 1). The high, low and average analyses are given in the following table.

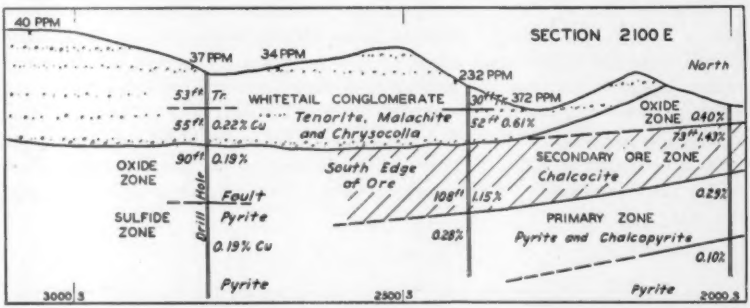

FIG. 3.

Mineralization	High copper, ppm	Low copper, ppm	Average copper, ppm
Capping over copper ore	2000	150	647
Pyrite mineralization	184	80	114
Unmineralized	68	Nil	31

Reverse Results.—Poor results were obtained on the steep slopes of a small section of the orebody which lies between the old No. 1 Mine and Amanda Gulch. Low soil assays occurred over the orebody and high assays occurred down the slope over barren capping. This hill was recently diamond drilled on 200 foot centers and has not been disturbed by mining. Soil samples were taken below palo verde trees to get a better pattern.

The southern end of the ore had been tilted up after the secondary orebody had formed. Recent erosion has cut part of the orebody away. The schist planes dip northward into the hill and there is some minor faulting with northerly dips. The copper released by oxidation and leaching probably migrated into the hill rather than straight down. The ore is thicker under the hill and is covered by more capping. There are copper stains in the bottom of the canyon due to incomplete leaching of the low grade ore (see Sect. 400E—Fig. 2).

Bedded Ore in Conglomerate.—Part of the Whitetail conglomerate south of Ray is cemented with copper minerals, tenorite, malachite and chrysocolla. Some of the ore beds outcrop, but most of the deposit is buried under barren conglomerate. Sulfide ore occurs in the bedrock below. Soil samples partly outline the ore even in areas where it is buried by as much as forty feet of barren beds. The deposit was later explored by diamond drilling (see Sect. 2100E—Fig. 3).

Mineral Creek Bed.—Relatively little copper was found in the trees growing in the bed of Mineral Creek below the orebody, although the creek drained the entire Ray mineral district. Soil below these trees consisted of sand and silt with very little organic matter. The decayed leaves and soil had been washed away by floods, so that the trees were unable to accumulate much copper.

Diabase East of Ray Fault.—Soil samples taken on mineralized outcrops east of Ray showed a "high" over the better mineralized areas, but the diabase assays were far higher than schist or granite porphyry assays for the same mineralization. Diabase and similar basic rocks retain more copper than the silicious rocks. In the Ray district an assay of 150 parts per million would be a favorable indication in leached schist capping, but it would take 400 parts per million or higher to indicate copper mineralization in diabase outcrops. Part of this area is covered by a thin cover of recent alluvium, which did not change the assay pattern.

CONCLUSIONS.

Geochemical prospecting can be a valuable geological tool and has great possibilities under favorable conditions. It can be an aid in outlining ore-

bodies, in selecting favorable areas for drilling and in eliminating unfavorable areas.

It does not take much copper to show up as a "high" in running trace assays. A little copper staining from a small deposit could give very erroneous results. The depth of overburden and the degree of leaching will also effect the results. The type of host rock is important, as small quantities of copper are more completely leached from siliceous rocks than basic rocks. Misleading results can be expected in regions that have been contaminated by smelter smoke.

Soil samples are as satisfactory as leaf samples and they are much easier to assay. Soil below oak, mesquite and palo verdi trees can be used.

ACKNOWLEDGMENTS.

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KENNECOTT MINING CORPORATION,
RAY, ARIZONA,
October 20, 1952.

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MORTON GRANITE GNEISS.[1]

ERNEST H. LUND.

ABSTRACT.

The Morton gneiss, one of a number of granites and granite gneisses referred to the Minnesota Valley granite series, is a hybrid gneiss with complexly contorted structure and variable color. Its hybrid nature is in part the result of lit-par-lit injection, but more important is the strewing out of numerous basic inclusions by the magma producing a "schlieren" gneiss. The contorted structure is probably the result of deformation during the late stages of solidification. Modal analyses show the composition more nearly quartz monzonite than granite.

INTRODUCTION.

THE granite gneiss quarried since 1884 at Morton, Minnesota (Fig. 1), is a distinctive stone that has become well known throughout the country. Its trade names such as "Rainbow," "Tapestry," "Antique," and "Variegated" granite are descriptive of its variations in color and texture and of its complexly contorted structure (Fig. 2).

The stone has been used as a base course in numerous large buildings including the Doherty-Cities Service Building in New York City, the Baker Building in Minneapolis, Daily News Building in Chicago, San Juanto Building in Houston, Federal Building in Los Angeles, Bankers Life Insurance Building in Des Moines, and Reforma 95, a large theater in Mexico City. The major part of the current production is used as polished facing stone for buildings and for monuments. The Naval Victory Monument on Guadalcanal is made from the "Rainbow" variety.

This stone was briefly described by Thiel and Dutton [2] and has been mentioned in earlier reports dating back to 1823.

QUARRIES.

In 1952 two companies, the Cold Spring Granite Company and the Melrose Granite Company, were operating at Morton (Fig. 1). Considerable prospecting for quarry sites has been carried on in adjacent parts of the Minnesota River Valley, and openings have been made in a number of places, but only the quarries in the vicinity of Morton, where the stone is of good quality and where railroad transportation is available, have maintained consistent operations.

The Morton quarry of the Cold Spring Granite Company is the largest in the Minnesota River Valley. The stone is quarried by channeling on all

[1] Published by permission of the Director, Minnesota Geological Survey.

[2] Thiel, G. A., and Dutton, C. E., The architectural structural and monumental stones of Minnesota: Minnesota Geol. Survey Bull. 25, pp. 88–94, 1935.

sides with pneumatic "drifter" drills. The "lift" is obtained by drilling horizontal holes six inches apart at the base of the block. Every third hole is driven half the distance of the others, and a light powder charge is placed in these shorter holes to break the block free at the ledge level. The blocks, weighing 50 to 80 tons, are hoisted from the quarry by a steel derrick with a capacity of 100 tons. They are transported on flatcars to Cold Spring,

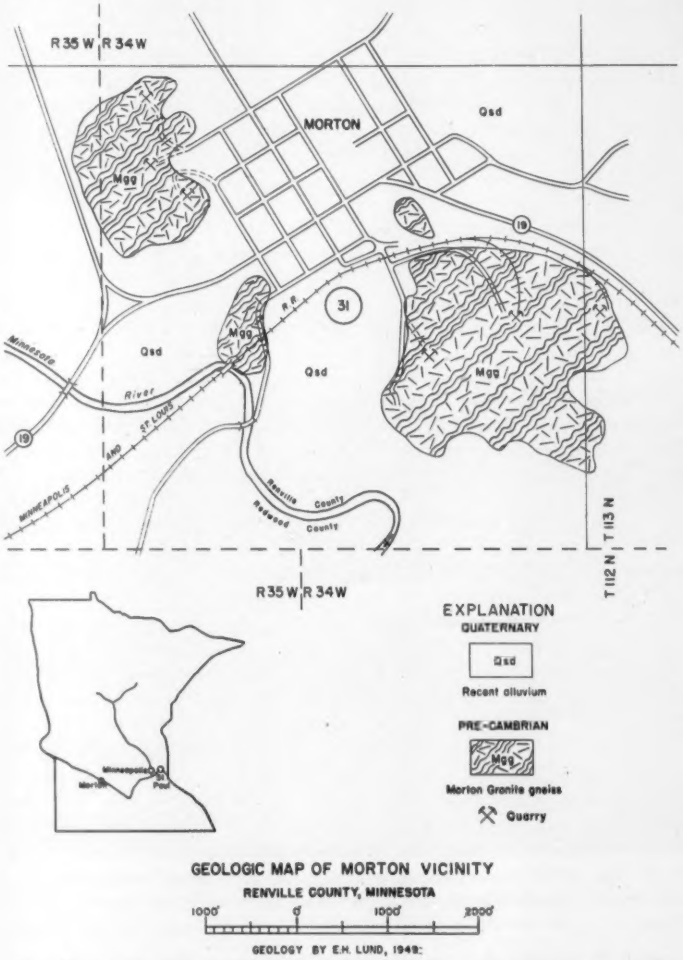

FIG. 1. Geologic map of Morton vicinity, Renville County, Minnesota.

Minnesota, where the stone is cut and finished. A large crushing and screening plant is operated on the quarry site, and the waste rock is utilized for crushed aggregate and poultry grit.

CHARACTER AND ORIGIN.

The Morton granite gneiss is one of a number of masses of granite and granite gneiss which are grouped in the Minnesota River Valley granite series.[3] These rocks occur in scattered outcrops between New Ulm and Ortonville. The Morton gneiss is the most widespread of the group, extending from near New Ulm to a point south of Sacred Heart, a distance of approximately 50 miles. Outcrops range from small knobs that protrude only a few feet above the river alluvium to irregular hills that rise as much as 100 feet above the valley floor. Most of the outcrops were scoured by the glacial River Warren, and the relatively fresh surfaces are marked by numerous potholes and scour channels. Locally the outcrops have a thin mantle of weather rock, and in places along the valley walls and along the streams tributary to the Minnesota River there are large thicknesses of residual clays that retain the structure of the parent granite gneiss.

The fresh Morton gneiss is variable in texture and color and has a highly contorted structure. These features are dependent upon the origin of the gneiss, which is a hybrid rock formed by the incorporation of a considerable amount of basic rock in a liquid granitic magma. There was considerable reaction between the basic inclusions and the magma, and the structure resulted from the strewing out of the incorporated materials producing what might be called a schlieren gneiss. The range in color from pink to dark gray likewise depends largely upon the degree of contamination of the granitic magma by basic rock. Generally the gneiss is coarse-grained, but locally it is very coarse or pegmatitic. The pegmatite masses commonly are dike-like in that they cut across earlier structures, but they appear to be streaks or segregations that disappear by gradation to medium- and coarse-grained gneiss.

In the vicinity of Morton, where the rock is quarried, the basic inclusions are generally small, and a large amount of material was incorporated in the granite with considerable reaction. A combination of processes probably produced the complex structure of the rock, but the most important was the incorporation of foreign material resulting in the formation of schlieren. Reactions between the basic inclusions (Fig. 3) and granitic magma developed shells of biotite on the inclusions. Movements and attrition caused the biotite to scale off, and the inclusions were reduced to pod-shaped masses. During this process the smaller inclusions, heated by the magma, probably were in a plastic condition, and it seems likely that by plastic yielding and by attrition many of the inclusions were completely destroyed and assimilated in the granitic liquid, the composition of which was appreciably modified as a result. Turbulence in the moving magma may have been the cause of the contorted

[3] Lund, E. H., Igneous and metamorphic rocks of the Minnesota River Valley, Ph.D. Thesis, University of Minnesota, June 1950.

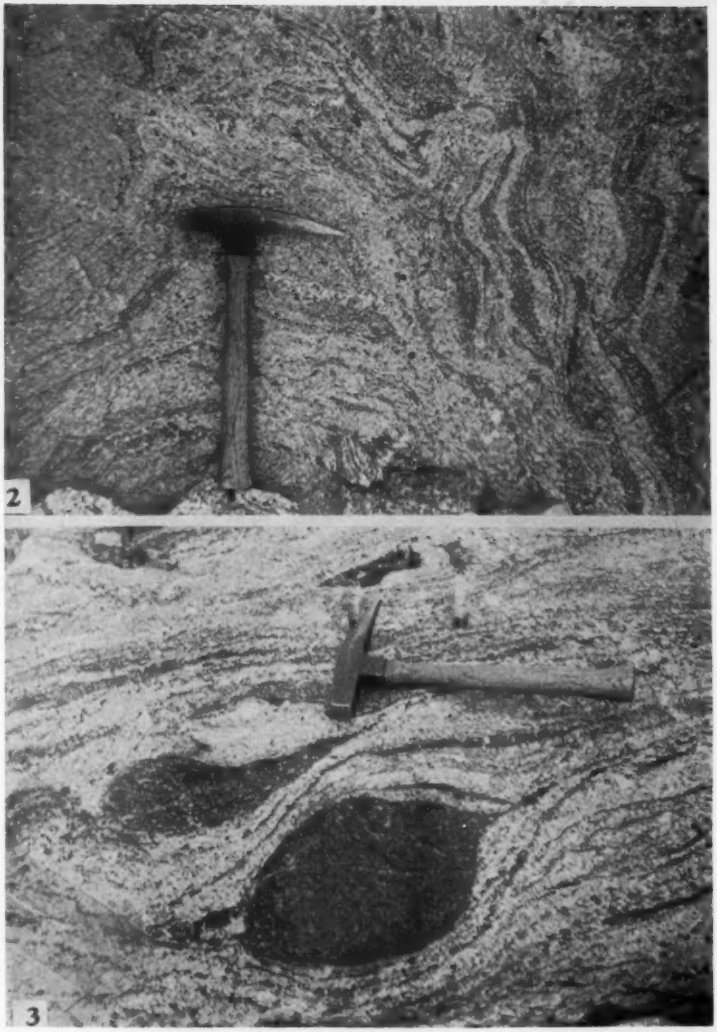

FIG. 2. Contorted Morton gneiss.
FIG. 3. Basic inclusions in Morton gneiss.

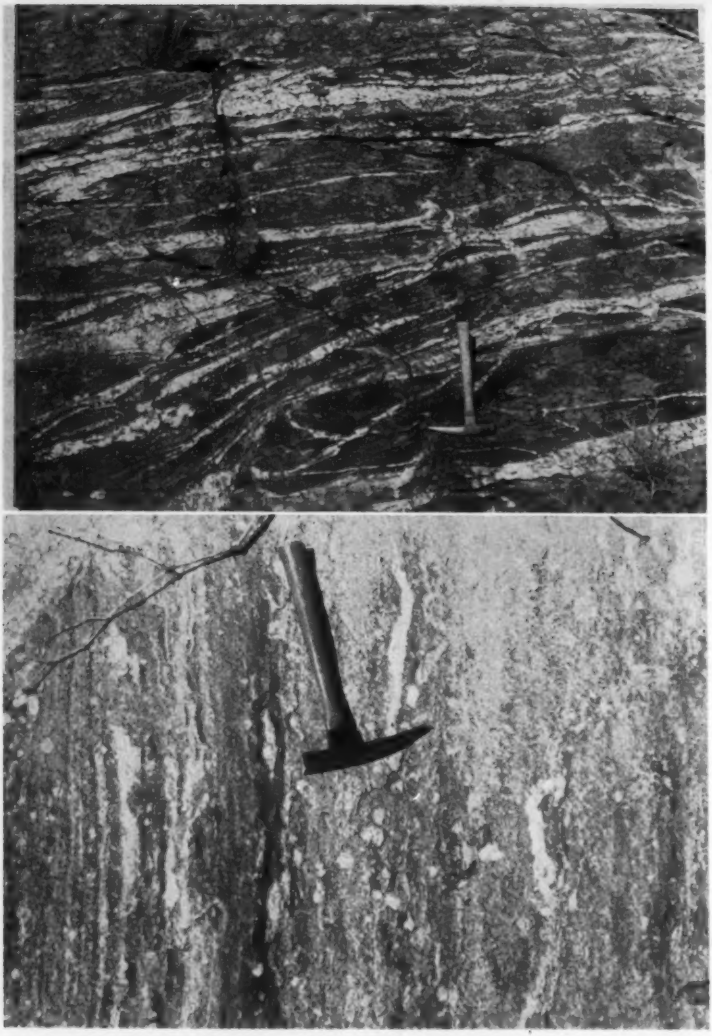

FIG. 4 (upper). Lit-par-lit injection of granite stringers in basic inclusion.
FIG. 5 (lower). Lit-par-lit injection with development of metacrysts in basic inclusion.

structure (Fig. 2), but deformation during cooling when the magma was in large part crystallized probably was the principal cause. Ptygmatic folds in pink granitic stringers which cut the banded structure in gray gneiss indicate that deformation took place while the banded rock was still in a plastic condition. Offsets in small late "gash veins" resulted from deformation during the final stages of solidification, and a small amount of granulation with development of mortar structure took place after complete solidification.

The inclusions range in size and shape from the small pod-like masses to large irregular blocks, some of which are 100 feet or more on the surface. Many of the larger inclusions show lit-par-lit structure with closely spaced

TABLE 1.

MODAL ANALYSES OF MORTON GNEISS.

(Volume percentage.)

	1	2	3	4	5	6	7	8	9	10
Potash feldspar	2	2	2	trace	2	50	51	32	35	44
Plagioclase	57 (An_{30})	57 (An_{32})	50 (An_{28})	60 (An_{32})	60 (An_{32})	9 (An_{18})	14 (An_{18})	30 (An_{31})	32 (An_{28})	25 (An_{31})
Quartz	24	27	34	32	30	39	34	37	27	26
Biotite	14	11	12	7	5	X	X	X	5	4
Accessories:	3	3	2	1	3	2	1	1	1	1
Magnetite	X*	X	X	X	X	X	X	X	X	X
Apatite	X	X	X	X	X	X	X	X	X	X
Zircon	X	X	X	X	X	X	X	X	X	X
Sphene	X	X	X	X	X				X	
Epidote	X	X	X	X	X	X	X		X	
Allanite	X	X	X	X	X		X			
Hornblende	X	X	X		X				X	
Muscovite		X	X						X	

1. Gray facies—tonalite.
2. Gray facies—tonalite.
3. Gray facies—tonalite.
4. Gray facies—tonalite.
5. Gray facies—tonalite.
6. Pink facies—leucogranite.
7. Pink facies—leucogranite.
8. Pink facies—quartz monzonite.
9. Mixed pink and gray—quartz monzonite.
10. Pinkish-gray—quartz monzonite.

X* Present in quantities less than 1 percent.

discrete stringers of granite (Fig. 4). In other inclusions the lit-par-lit injection is less distinct, and the action of the magma on the inclusions was more pervasive (Fig. 5). In some of these masses feldspar metacrysts an inch or more long were developed, giving the rock the appearance of augen gneiss. The inclusions are variable in composition, texture, and structure. In large part the variations in composition can be related to size, and this suggests that the variations in composition are due mainly to reaction between inclusions and the magma rather than to differences in the original rock. Thus, there is a tendency for the larger inclusions to be more basic ranging from dioritic to gabbroic in composition; whereas the smaller inclusions are generally more

silicic. Pyroxene, calcic andesine or labradorite, and a small amount of hornblende make up the large inclusions; hornblende, and andesine or oligoclase with little or no pyroxene are typical of the smaller ones. Reactions of inclusions with the granitic magma proceeded in accordance with Bowen's reaction principle. As the smaller inclusions were disintegrated, the hornblende was recrystallized to biotite, and the foreign material lost its character as inclusion to become an integral part of the gneiss. In general the inclusions are sugary-grained; some are masssive and others have a definite gneissic structure.

The mode of origin of the Morton gneiss which has been outlined above suggests that variability in composition is to be expected. Locally where inclusions are numerous and a large amount of ferro-magnesian minerals were incorporated, the resulting gray gneiss is characterized by calcic oligoclase. The gray gneiss alternates with bands of pink rock which contains potash

TABLE 2.

CHEMICAL ANALYSIS OF MORTON GNEISS FROM COLD SPRING GRANITE COMPANY QUARRY.

SiO_2	71.54
Al_2O_3	14.62
Fe_2O_3	.69
FeO	1.64
MgO	.77
CaO	2.08
Na_2O	3.84
K_2O	3.92
H_2O+	.30
H_2O-	.02
CO_2	.14
TiO_2	.26
P_2O_5	.10
MnO	.04
	99.96

S. S. Goldich, analyst, in The Architectural, Structural and Monumental Stones of Minnesota, Minnesota Geol. Survey Bull. 25, p. 90, 1935.

feldspar. This pink rock generally is coarse-grained and often pegmatitic. Modal analyses of 10 specimens of the Morton gneiss, given in Table 1, range in composition from that of a light-colored granite (leucogranite) to quartz diorite (tonalite). The average of the modal analyses gives quartz, 31; potash feldspar, 22; oligoclase, 39; biotite, 6; and accessory minerals, 2 percent. The accessory minerals are magnetite, apatite, zircon, sphene, allanite, hornblende, and muscovite. The average composition from the modal analyses closely approaches an estimate made by Goldich [4] from chemical and mineral analyses of the rock in the Cold Spring quarry. The chemical analysis is given in Table 2. The average composition indicates that the rock is more nearly a quartz monzonite than a granite.

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July 16, 1952.

[4] Goldich, S. S., A study in rock weathering: Jour. Geology, vol. 46, pp. 38–58, 1938.

STEATITE DEPOSITS OF BHERAGHAT, JABALPUR DISTRICT, M. P., INDIA.

V. N. CHHIBBER.

ABSTRACT.

Steatite finds increasing use in so many industries that it is classed as a critical mineral. This is the only occurrence of steatite in Madhya Pradesh that has been exploited on a commercial scale. Its importance is further enhanced in view of the many uses to which this commodity adapts itself, due to its physical characters—extreme fineness, softness and freedom from grit. The steatite occurs in the neighborhood of Bheraghat in the form of compact foliated masses, in irregular lenticular pockets and veins occurring in a magnesium marble. The megascopic and microscopic characters of the various varieties have been described. Moss talc is reported for the first time from India. Basic igneous rocks were intruded into this marble, followed by a hydrothermal phase containing silica in solution which gave rise to quartz, geode quartz, chalcedony, and agate, in the form of veins and patches in the marble. Of the constituents of steatite, silica and water were provided by the hydrothermal waters, and the magnesia was undoubtedly supplied by the dolomitic marble. Tremolite and anthophyllites are the other contact facies. The methods of mining, labor and transport, grading of steatite, exports, and the uses to which the steatite is put, are discussed in detail.

INTRODUCTION.

A SAMPLE of steatite from this locality examined by F. R. Mallet [1] in 1889 was described as "white, with pale reddish blotches here and there; somewhat schistose." He made this observation in connection with studying the possibility of exporting this mineral to London, if it could compete with the costly steatite then being obtained from Germany. Later, in 1909, L. L. Fermor [2] while referring to this occurrence, stated that the steatite formed steeply dipping pockets in the Dharwarian dolomites. In 1915, Holland, Hayden and Fermor [3] in Quinquennial Review of Mineral Production of India (1909–13) record: "The steatite deposits on the north side of the Marble Rocks in the Jubbulpore district, which were formerly worked by native methods with a small annual production, have now been taken up on mining lease by Messrs P. C. Dutt and Burn & Co. . . . while deposits at Gowari and Lalpur on the south side of the Narbada have been secured by the Bombay Mining and Prospecting Syndicate." Dr. H. L. Chhibber [4] made a preliminary study of these

[1] Mallet, F. R., Note on Indian steatite: Rec. Geol. Survey India, vol. 22, p. 64, 1889.

[2] Fermor, L. L., Minerals of the Jubbulpore district, C. P.: Jubbulpore District Gazetteer, A, p. 263, 1909.

[3] Holland, T. H., Hayden, H. H., and Fermor, L. L., Rec. Geol. Survey India, vol. 44, p. 291, 1915.

[4] Chhibber, H. L., Proc. Ind. Sci. Cong., p. 56, 1945.

deposits and an abstract of his work was published in the Proceedings of the Indian Science Congress. Later, while dealing with the steatite resources of India [5] he again referred to this occurrence of the mineral in Madhya Pradesh.

It may be noted that this is the only occurrence of steatite in Madhya Pradesh that has been exploited on a commercial scale. The deposits are important economically because of the many uses to which this mineral adapts itself, due to its physical characters of extreme fineness, softness, and freedom from grit. Talc is finding an increasing use in many industries and Indian steatite is exported to the United States. It is therefore an important dollar earning mineral. In this communication are given the results of a detailed investigation of these deposits, carried out by the author during 1948 and 1949.

Bheraghat (23°7′50″:79°48′1″) is 13 miles from Jabalpur by road and 3 miles from Mirganj Railway Station on the Central Railway, both of which are connected with Bheraghat by metalled roads.

OCCURRENCE.

It is noteworthy that deposits of talc are found associated with a magnesian marble of Bheraghat. The steatite occurs in compact foliated masses, and is found in irregular lenticular pockets and veins in this marble. The localities where steatite occurs are, (1) Bheraghat, (2) Gwari, (3) Lalpur, (4) Darwara. The most important locality is Bheraghat. The Bheraghat occurrences lie on the right bank of the Narbada river and the other three localities are across the river.

MEGASCOPIC CHARACTERS.

Color.—The mineral is generally white, but it is also yellowish, pinkish, dirty brown, greenish (sea-green), or even grayish in color. The first grade variety is white, or it may have a greenish tinge; the second is yellowish and the third grade is yellow in color. The lower grades of steatite are grayish and in places dirty brown in hue. It may be noted that the color of a particular specimen of steatite becomes much clearer when dipped in water. This phenomenon was observed when determining the specific gravity of the different varieties of steatite.

Moss Talc.—An interesting specimen of moss talc was collected from Bheraghat which shows dendritic dark inclusions in a body of yellow talc. Another specimen shows a beautiful development of black dendritic patterns in pinkish talc. These moss-like inclusions become clearer when the specimen is rubbed with a little vegetable oil. So far as the author is aware, moss talc has not been described from India before.

Streak.—The streak of the talc varies with the color. The white specimens yield a white streak, as do the pale sea-green variety. The others give a streak corresponding to their color.

Hardness.—The hardness of this steatite is variable; when pure it is fine-grained, smooth and soft with a hardness of 1. When somewhat impure, it is

[5] Chhibber, H. L., India, Part III, Advanced economic geography of India and Pakistan, pp. 247–248, Nand Kishore & Bros., Banaras, 1949.

slightly harder, e.g., when intermixed with marble. The lower grade steatite is also slightly harder. The mineral cuts easily along the foliation, but with difficulty across it.

Cleavage and Luster.—This steatite has a good cleavage and readily breaks into small inelastic flakes. On cleavage surfaces the luster is splendent silky (pearly).

Specific Gravity.—The specific gravity of the different varieties of steatite was determined to vary from 2.67 to 2.81.

Action of Acids.—The steatite is not decomposed by acids.

MICROSCOPIC CHARACTERS.

Thin sections of varieties of steatite were seen under the microscope to be composed of colorless elongated sections of talc with irregular edges. In

FIG. 1. Photomicrograph of anthophyllite schist from near the *Dhuan Dhar* Falls. The anthophyllite has developed at the contact of the basic igneous intrusion and the marble. The prismatic crystals of anthophyllite (with parallel extinction) form a schistose aggregate. (Photomicrograph by V. N. Chhibber.)

places, only tiny flakes or elongated needles are to be observed and these are colorless with micaceous cleavage. In some places the flakes of talc have a radiating arrangement, and in others there are cross-shaped aggregates. The mineral has a twinkling effect when the stage is rotated and exhibits bright pink, greenish blue and yellow polarization colors of the second order. It has straight extinction (Fig. 1). The birefringence, however, seems to vary, as in places lower polarization colors are observed.

A thin section of a specimen collected near Bheraghat was observed to be composed almost wholly of talc; only a few other minerals are found associated.

Dolomite is observed to occur in irregular patches. It is noteworthy that the mineral has a very irregular outline, having deep embayments in places. In some places flakes of talc are seen penetrating dolomite, showing that the talc has been formed by the replacement of dolomite. Fine, irregular, microscopic inclusions of talc are observed, some of which are visible only under high power. The section on rotation shows a very marked twinkling effect.

A prismatic section of a colorless mineral with a well-marked outline shows an extinction angle of nearly 46°. It contains tiny inclusions of talc. It appears to be diopside, which has developed along with steatite. A few grains of zoisite and epidote are also present. They occur in tiny irregular grains visible under high power. There are a few very tiny grains of a mineral with a blue color, having a high refractive index with distinct and strong pleochroism. It appears to be glaucophane.

ORIGIN OF STEATITE.

The origin of the talc and tremolite is bound up with the history of igneous activity of the area. Intrusions of basic rocks comprising different fine-grained types of gabbro, dolerite, and epidiorite occur in the marble, and have been described in a separate communication. This activity was followed by a hydrothermal phase carrying silica in solution, and there is abundant deposition of quartz, geode quartz, chalcedony, and agate, in the form of veins and patches in the marble. Of the constituents of steatite, silica and water were provided by the hydrothermal waters, and magnesia was undoubtedly supplied by the dolomitic marble. Where the marble contained both lime and magnesia, tremolite was the contact mineral developed. Where both magnesium and iron were present, anthophyllite has been formed, as seen in anthophyllite-schists developed at the contact of the basic intrusion and the marble.

TECHNOLOGIC CONSIDERATIONS.

The talc is quarried seasonally by agricultural labor in open cuts, which range in size from 25 to 300 feet in depth and 9 to 50 feet in width.

The steatite is exported from Mirganj Railway Station. The author was informed that The Katni Cement Co. has a large quarry at Bheraghat and that the life of a large pit may be 20 to 25 years. Five to six small quarries were being worked at the time of author's visit in December 1948, and in one quarry an average of about ten laborers was employed. Some of the pieces of talc extracted measured more than two feet in size. An additional seven to eight quarries were also being worked at the same time in the distributary channel, described above. The total output varies from 20 to 40 maunds a day. The work is carried on only in the open season.

The steatite is graded according to its color and purity. The prices of the different grades prevailing in January, 1949, are given below:

1. The first grade comprises white or light sea-green steatite which fetches Rs. 90/- to Rs. 100/- per ton at Mirganj R. S. When this material contains flakes of muscovite it lowers the quality and consequently the price.

2. The second grade is white or whitish in color. Its price is Rs. 70/– to Rs. 80/– per ton.

3. The third grade has a yellowish tinge and its price varies from Rs. 30/– to Rs. 50/– per ton, with an average of Rs. 40/– per ton. The lower grade talc is grayish in color and is poor in quality. These are the recognized grades, but still inferior qualities are also known.

The block steatite is used locally for various ornamental articles, for talcum and toilet powder, in textiles, for polishing rice, *arhar dal,* wood and in the manufacture of paints, paper and rubber goods. It is also used as an adulterant in soap manufacture and as a lubricant. Soapstone slabs are employed for hearthstones, switch-boards, sinks, laboratory tables, wash tubs, acid tanks and furnace linings. Exported steatite is used for many articles such as radio tube bridges. After firing, these are harder than steel.

ACKNOWLEDGEMENTS.

The author offers his thanks to Dr. H. L. Chhibber for his guidance. He takes this opportunity to express his sincere thanks to Mr. D. K. Chakravarti for having gone over this manuscript.

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November 3, 1952.

DISCUSSION

BANDED HEMATITE QUARTZITES

Sir: More has been written about the banded hematite quartzites (or whatever favorite name a particular author may care to use) than most other specialized rock types. Some may feel that there has been a surfeit of such papers. But it is very fitting that Drs. Spencer and Percival should write their views [1] on these rocks in India where they have spent so many years. Those views are of considerable interest, and no doubt will receive wide attention.

Before commenting on the facts and interpretations presented, it is advisable because of the importance of the paper to clear two ambiguous remarks.

Firstly, on page 369 there is the following statement: "and, indeed, after we had pointed out the incorrect placing of the 'basal' conglomerate in the Geological Survey publications (which was originally based on correlations further afield), Dunn entirely revised the succession in the area."

The revision of the succession in South Singhbhum was made in 1938 consequent upon my detailed re-mapping of part of that area. The reasons for the re-survey were first given elsewhere.[2] The re-survey was of an area previously mapped by Jones of the Geological Survey of India in 1920–22. Jones, Percival and Spencer had each referred to conglomerates (in the area of the Iron-ore Series in South Singhbhum) other than those which were thought to be at the base of the Series, but nobody was clear on them or produced a map of them. Indeed, in 1931, Percival wrote,[3] "Further investigation may show that all of these conglomerates are of one horizon, much newer than the 60 foot sequence of sandstone and conglomerate at the base of the Iron-ore Series." This confused matters and obviously accepted the "60 foot sandstone and conglomerate" as the base of the Iron-ore Series; in the event, the re-survey showed that the "sandstone and conglomerate," which had been thought to be the base of the Iron-ore Series, was the base of a very much younger series (the Kolhan Series), resting with strong unconformity over the Iron-ore Series. The crux of the whole problem was found to be right along the northern doorstep of the Noamundi iron-ore lease on which Percival worked for so many years—one week's mapping in the long years between 1922 and 1938 would have cleared up the problem.

It is of interest to note that this unconformity between two groups of Precambrian rocks is so excellent and so clearly exposed that, when it became

[1] E. Spencer and F. G. Percival, Econ. Geol., vol. 47, 1952, pp. 365–383.

[2] Records Geol. Surv. India, 73, p. 27, 1938, and in greater detail in Mem. Geol. Surv. India, LXIII (3), pp. 303–305, 1940.

[3] Trans. Min. Geol. Inst. India, XXVI, p. 261.

necessary to introduce field training camps for Geological Survey recruits, I chose this area for part of their training.

The second ambiguous remarks by Spencer and Percival is made by way of a quotation from a paper of mine written in 1935, and a statement by the authors. They quote (p. 366)—"He (Dunn) says, 'the immediate neighborhood of the larger iron ore deposits in Singhbhum provides little evidence to support any theory of their origin. A wider survey over several thousand square miles of country demonstrates that the associated banded quartzites are not sedimentary, but are due to secondary silicification of material now represented by ferruginous, chloritic, or carbon shales or phyllites, many of which originated as tuffs.'"

They then state (p. 369) ". . . we do not agree at all with Dunn's secondary silicification theory, *nor do we see any necessity to go to localities far away from these banded rocks to seek their origin.*"

I have italicized the critical words. My views on contemporaneous silicification were formed after many years of mapping, over several thousand square miles of country containing many occurrences of these banded hematite rocks. These views were not formed in "localities far away from these banded rocks"; the localities of the banded quartzites on which my views were developed may have been some distance from the Noamundi-Jamda area in South Singhbhum, of which Spencer and Percival write, and the occurrences in these localities are not as extensive in outcrop as in South Singhbhum; but when my detailed mapping was later extended to the latter area evidence of silicification was found there also. I will refer again to this later.

I have specifically drawn attention to the above two ambiguous statements by Spencer and Percival, for they illustrate a difference in fundamental outlook. The basis of geological work is field mapping; without it all the discussion in the world is likely to lead nowhere. My own views were developed only after many years of detailed mapping and petrological work (much microscopical work being done from day to day in camp), following the rocks through all their phases. The detailed maps of the Geological Survey of India have always been available to those interested. It is true that much of the evidence which went to form my own views is to be found in places not readily accessible. Nevertheless, the evidence provided by these banded quartzites and their associated rocks is described abundantly enough in various writings.[5] The articles in ECONOMIC GEOLOGY [6] could only present the conclusions. Such a mass of evidence cannot be brushed aside in references to the South Singhbhum rocks by the statement that "we do not agree at all with Dunn's secondary silicification theory."

I would now make some comments on the descriptions presented by Spencer and Percival and on their interpretations.

Concerning their comment on the name "banded hematite quartzite," all who have written on these rocks have appreciated their similarity to other

[4] Mem. Geol. Surv. Ind., LXIII (3), 1940.

[5] Memoirs of the Geological Survey of India, 54, 1929; 69, part I, 1937; 59, part 2, 1942 particularly; and 63, part 3, 1940.

[6] Vol. 30, pp. 647–654, 1935; vol. 36, pp. 355–370, 1941.

rocks of varied designations in other countries. I have expressed a preference for "banded jaspers," but recognizing that they *are* (contrary to Percival and Spencer) considerably recrystallized in many parts of the extensive area over which I have examined them, the term "banded hematite quartzite" first used by someone many years ago, has stuck and might as well stay.

In general, I would agree with most of the two authors' descriptive detail. There would be differences of opinion of the relative abundance of certain features according to personal experience. For example, the statement that "as a rule, even when highly folded, the jasper bands have fractured biscuit-like" seems to me to be an over-emphasis of such fracturing; this over-emphasis is apparent also in other structures described, such as the "spherulites." It would, however, be impossible for me to accept the following description (p. 382): "The Indian banded rocks appear to have been less altered from their original condition than those in many other areas. The beds have been folded to a moderate degree but . . . the pressures . . . have not been so great as to recrystallize either silica or the iron oxides." This statement of "moderate" folding and lack of recrystallization does not fit the facts as provided in the Geological Survey of India Memoirs. There are certain parts of the Singhbhum region in which severe folding in the Iron-ore Series is not so evident, but over the greater part of the area in which the banded hematite quartzites and associated rocks occur (and including the Noamundi-Jamda area of South Singhbhum) they have been acutely and closely over-folded—indeed folding has been so intense that part of the much later Kolhan Series has been overfolded with them. The banded hematite quartzites have in several areas been recrystallized to quite coarse quartzitic rocks and to hematite-quartz schists. Their metamorphism to grunerite-magnetite rocks in places seems to have been due rather to other factors in metamorphism than to pressure.

It is on the interpretation of descriptive matter that I would differ mainly. The authors have referred to a clear-cut division between (a) plastic deformation and (b) shatter folding in the banded hematite quartizites, suggesting that the former took place while the rock was in an unconsolidated gel condition. Of course several possible causes could be advanced to explain movement while such rocks were in an unconsolidated condition, including slumping and slip-bedding. (It may be pointed out here, that such movement would just as likely take place in beds being replaced by silica contemporaneously with deposition as in beds of silica gel deposited directly as such.) However, in my experience, the distinction made by the authors of the type of folds is artificial. It is my experience that the "shattering" is relatively minor in amount compared with the close unfractured folding. But one can commonly follow a fold, in one place unbroken, in another fractured—there is no clear-cut distinction. The folding is integral with the close regional folding which is so evident in the Iron-ore Series. Jones has some very fine photos of folding in the banded hematite quartzites in his Memoir Geol. Surv. India, LXIII. It would be impossible for me, from my regional mapping, to accept such an origin for the close folding as that suggested by Spencer and Percival —I would not deny the possibility that there may be some distortion having

the origin they suggest, but to prove this in such an area of intense folding would be difficult.

The occurrence of magnetite and of carbonate pseudomorphs in the banded hematite quartzites has been previously described from time to time. These minerals occur also in the associated cherts, and in the associated chloritic, sericitic and carbon phyllites (described in my various Memoirs G. S. I.). They are of no greater significance in postulating either a sedimentary or a replacement origin for the silica. There is nothing in the authors' descriptions that is opposed to replacement; on the contrary, their descriptions (as distinct from interpretations) indicate that there has been some replacement.

On page 377 certain of the features described (which are not disputed) are given interpretations which would be disputed by many. Why should it be "difficult to believe that the above structures, with their accompanying shrinkage cracks, have been formed by rearrangement or replacement after the complete consolidation of the material"? One interpretation amongst others may indeed be recrystallization.

Again, why would it (p. 377) "appear to be equally improbable that such delicate textures as shown by these spherulites and micro-shrinkage cracks, could have persisted through any marked degree of metamorphism of the containing banded jaspers, and it would follow that the beds in which they occur could have not suffered any appreciable metamorphism since their consolidation"? In the first place, the authors' views on the origins of the "spherulites" and so-called micro-shrinkage cracks are just assumptions (there are other views); in the second place petrology is full of examples of so-called "delicate" textures being preserved through more severe stages of metamorphism than even these rocks have undergone—such examples are abundant in other rocks of Singhbhum (e.g., the amygdules in the recrystallized lavas).

The authors' suggested relation of puckering to movement in an unconsolidated gel is but a suggestion, quite unproved, yet we find on page 381 the categorical statement: "But whatever the initial cause of the banding, the local puckering and crumpling of these rocks were undoubtedly brought about when the material was still in a soft or plastic state."

One assumption after another is made and the whole built into a structure having an air of solidity, but in reality as stable as a house of cards. We are all, perhaps, prone to this in our enthusiasms unless we are careful, and indeed the changing picture in geological emphasis down the years is largely because of it.

Perhaps I may now conclude with a brief review of my thoughts on these rocks—in the nature of a valedictory, for it is unlikely that my duties now and in the future will again permit me the opportunity to return to such discussions.

I have long held the view that if whatever I have written cannot stand on its own legs, well then it is not worth defending, but it is reasonable that the evidence provided should be read and weighed. My own uncertainties on the origin of the banded hematite quartzites of South Singhbhum (the area of which Spencer and Percival write) are clearly expressed elsewhere.[7] It will

[7] Memoir Geol. Surv. India, LXIII (3), pp. 336–338, 1940, and in ECONOMIC GEOLOGY, vol. 36, pp. 355–370, 1941.

be seen there how hesitant I have been in accepting any but a direct sedimentary origin for the extensive banded hematite quartzite of South Singhbhum, but how the great weight of evidence of silicification, accumulated over the years within the thousands of square miles of the Iron-ore Series mapped in all parts of Singhbhum and surrounding country, could not be ignored, and was not disproved by any evidence in South Singhbhum, and where indeed there is ample evidence of silicification.

Briefly, the belief formed from the accumulated evidence is that these banded rocks were deposited as sediments and tuffs which were exposed to sub-aerial conditions during accumulation; iron silicates and perhaps carbonates were converted to oxides, and, with widespread resorting, such oxidized material also gave rise to fine ferruginous sediments. It was a period of volcanic activity, and the sediments and tuffs, contemporaneous with their deposition (that is, while still unconsolidated), were silicified by the activity of thermal waters soaking through them and close to thse surface, thus giving rise to the banded hematite quartzites and other cherty rocks. I must accept the observed evidence of the replacement origin of these rocks in many parts of Singhbhum and adjacent areas, as long as modern criteria of replacement are accepted. Should there be a marked change in the general acceptance of what are the criteria for replacement, then also, the accumulated evidence in Singhbhum would require review. Like Spencer's and Percival's views which, as pointed out above, are built up on a series of inferences, my own views are founded on inference—the generally accepted inference implied in criteria of replacement.

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REVIEWS

Contribution à l'Étude des Gîtes de Tungstène Français. By MAURICE WEPPE (1951). Puy-Les-Vignes (Haute-Vienne), La Chataigneraie. Géologie Appliquée et Prospection Minière. Bulletin de l'Association des Ingénieurs Géologues de l'Université de Nancy. Société d'Impressions Topographiques, pp. 1–207, figs. 1–43, pls. 1–8.

The tungsten deposits described are located in south central France in the Department of Haute-Vienne, 22 km east of Limoges, and in the Department of Cantal, near Leucamp, 18 km southeast of Aurillac. The first, Puy-Les-Vignes, is situated in an area of gneissic and schistose rocks lying between two large granitic areas some 6 km apart. The second, at Leucamp in the region known as La Chataigneraie, lies in an area of mica schist close to a granitic mass.

The two are mining areas about 150 km apart. Puy-Les-Vignes is a nearly vertical chimney-like deposit with workings extending to 195 m. The chimney is offset by a vertical fault and several steeply inclined nearly parallel veins cut the chimney. Leucamp is an area of comparatively small veins oriented 80°, 60°, 40°, 20° NW, NS and N 20° E. The veins mined lie along the N 40° W trend and vary from 20 m to 40 m in length.

Quartz is the dominant gangue mineral of both areas and wolframite the principal source of tungsten. Tourmalinization is a prominent border effect in the schist and in places occurs in the veins as well. Sericite is prominent and kaolinization is mentioned. The two deposits probably formed after the major part of the Hercynian and before the Stephanian.

Wolframite occurs in crystals from 0.5 to 20 cm long, some of which are terminated. The analysis is WO_3—76.3; MnO—3.51; FeO—21.5. Associated minerals are ferberite, scheelite, pyrite, arsenopyrite, chalcopyrite, bismuth and bismuthinite. At Puy-Les-Vignes an isolated galena-bearing quartz vein is reported on the bottom level.

Some siderite occurs with the ore and in places contains associated ferberite. Large crystals of "reinite" having the form of scheelite are described. Veinlets of ferberite cutting scheelite are also illustrated.

Numerous microphotographs show the textural relations of ore and gangue minerals in the deposit. It would appear from these that tungsten precipitation followed tourmalinization and that wolframite was produced during the earliest stage of tungsten mineralization. Arsenopyrite followed wolframite and was in turn followed by ferberite. Scheelite may have been essentially contemporaneous with wolframite, but was localized more or less in the siderite areas. Veinlets of adularia cut scheelite but have been obliterated in part by ferberite. Small amounts of rutile are associated with the adularia. Arsenopyrite preceded pyrite in part, which was in turn followed by chalcopyrite where the latter is present. Bismuthinite is also a later sulfide. Native bismuth cuts arsenopyrite, follows fractures in wolframite and may be seen penetrating cleavages in bismuthinite.

In the earliest stage of mineralization quartz, tourmaline, and apatite were formed with the removal of Na, Ca, K and the addition of Si, Al, Mg, Fe, B and P.

In the ore-forming stage wolframite, scheelite, arsenopyrite and pyrite were formed with the addition of W, Mn, Fe, Ca, As, and S. Solutions in a post ore stage deposited adularia, siderite, rutile and reinite, with the subtraction of Mn, Ca and the addition of Si, Al, K, C, Fe and Ti. At a later stage quartz, bismuthinite, bismuth, chalcopyrite and sphalerite were introduced with the addition of Si, Bi, Cu, S and Zn. The last two stages marked the formation of (1) vein orthoclase with mica and (2) galena with the introduction of K, Al, Si, Pb and S.

The author has provided a most useful account of these historical tungsten occurrences, Puy-Les-Vignes at least being known since the close of the 18th century. The interpretations of the structure, mineralization and history of formation provide an account well worthy of close comparison with descriptions of tungsten deposits in the United States.

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December 1, 1952.

Géologie des Gîtes Minéraux Marocains. Service Géologique du Maroc Mém. 87, Casablanca, 1952. Pp. 416; pls. 23; figs. 48. Price, Fr. 2,000.

At a time when considerable interest is being directed toward North Africa's mineral resources, this book appears most opportunely. Prepared by the leading members of the Moroccan Geological Service, it contains discussions and descriptions of the geology of Morocco's mineral deposits. The minerals under consideration are: tin, tungsten, molybdenum; manganese; uranium; cobalt, nickel; iron; antimony; copper; lead, zinc; silver; gold; vanadium, bismuth, chrome titanium, arsenic; coal; petroleum; phosphates; graphite; fluorite; mica; beryl; asbestos, gypsum, salts; clays and miscellaneous minerals. The contributors include: J. Agard, J. Bouladon, J. Destombes, A. Jeannette, G. Jouravsky, R. G. Lévy, W. Van Leckwijck, Ph. Morin, J. Marçais, R. Moussu, B. Owodenko, F. Permingeat, and H. Salvan.

Each of the minerals or mineral groups is analyzed according to the district in which it is found, the mineralization of the district, types of deposits, origin, chemical analyses of deposits, and many very well-prepared maps showing the distribution of the minerals under discussion in relation to the geology of the country, and conclusions as to future prospects for development.

The book is extremely well organized both from the standpoint of clarity of presentation and thoroughness of preparation. It is the most comprehensive study yet to appear on the mineral resources of Morocco and will be of great interest and value to anyone seeking information on this subject.

B. A. BROMBERT.

NEW HAVEN, CONN.,
December 1, 1952.

The Geology of Hong Kong. By S. G. DAVIS. Pp. 210; 35 plates and maps. Government Printer, Hong Kong, 1952. Price, 35 Hong Kong dollars.

This is a complete and detailed account of the geology of Hong Kong and the New Territories, covering some 396 square miles. It is in part based upon the previous work of R. W. Brock, T. L. Phemister, S. J. Schofield, W. L. Uglow, and M. Y. Williams. Doctors Brock, Uglow and Schofield died before their reports were complete.

The book gives the physical features, a summary of the geology, a chapter on stratigraphic and petrographic details, paleontology, geologic history, orogenic

movements, chemistry of the igneous rocks, soils, archeology, rock analysis and bibliography. The chapters on economic geology deal with the larger features of mineralization and deposits of lead, silver, iron ore, tungsten, tin, molybdenum, graphite, gold, feldspar, building materials, coal and clays. Lead, iron ore, and clays constitute the important deposits.

This book is nicely written, well illustrated and should be of interest to geologists, civil engineers, geographers and archeologists.

Risorse Minerarie dell'Africa Orientale, Eritrea—Ethiopia—Somalia. By LUIGI USONI. (Under the auspices of the Ministry of Italian Africa.) Pp. 553; figs. 128; tbls. 5. Jandi Sapi Editori, Rome, 1952. Price, 5,000 lire.

The current crop of books dealing with Africa has yielded yet another, this one being a highly detailed study of the mineral resources of East Africa. It is not surprising that it should be the work of an Italian geologist, who treats the subject with minute preparation and intense feeling. Italy still looks upon Africa as the panacea for most of its economic ills and deeply regrets the loss of this territory. The author points with pride to Italy's accomplishments in East Africa, to the research, the mineral exploitation and development of mining techniques, and devotes a ten-page appendix to a discussion of the Colonial Mining Service set up at the time of the unification of Eritrea, Somaliland and Ethiopia under the Italian government. This service was organized for the purpose of uniting all mining activities in East Africa under one bureau so that geologists, mining engineers, technicians and investors might be coordinated in their work to promote more effective exploitation.

It would seem that there is no small quantity of mineral deposits yet to be developed in this region. The author, to prove this most clearly, has divided his book into four parts entitled: Metallic Minerals; Non-metallic Minerals, with a note on the salt mines of the coast and the interior; Building Materials, and an extensive review of Mineral and Thermomineral Sources. He begins the book with a brief survey of the general geology of East Africa and then delves directly into the subject of mineral deposits found in East Africa, the most important of which are iron and ferrous manganese, copper, tin, lead, gold, platinum and petroleum. To each of these, and the other minerals not mentioned, is devoted a chapter in which precise descriptions of the various locations, types of deposits, chemical analyses, tables of present development and potential production, maps, graphs, and more such pertinent data are given for each of the three countries earlier mentioned. The book is highly detailed and indicates the years of research, on the part of the author and his predecessors, that must have gone into its preparation. The skillfully written text is well illustrated with excellent maps and tables and many interesting photographs. Both the author and the publisher are to be warmly congratulated for producing so fine a work.

B. A. BROMBERT.

NEW HAVEN, CONN.,
December 1, 1952.

International Tin Study Group—1952 Statistical Year Book. By WILLIAM FOX, Secretary-General. Pp. 268. International Tin Study Group, The Hague, 1952. Price, $5.60.

This comprehensive volume is the second to be issued and far surpasses its predecessor of 1949. This volume appears in 17 sections, with an appendix. There are two main parts, one of general articles, Sections 1 to 8, dealing with international tin cooperation, trends in world tin production, consumption, uses,

stocks, prices, smelting, controls and trade. The second part gives figures on the production, consumption, imports, exports, alloys, tinplate and canning industry, for several years, of 110 different countries. There are included a group of useful maps of the Belgian Congo, Nigeria, Bolivia, Malaya, Thailand, and charts of tin production and trade in 1951, smelters of Europe and the use of tin in the United States.

The volume is a storehouse of statistical data and should prove of interest to all of those interested in the tin industry and trade in tin-containing goods.

Geologic Map of East Tennessee. Compiled by JOHN RODGERS. 14 maps, sections. State of Tennessee, Department of Conservation, Division of Geology, Nashville, 1952.

This volume, prepared in cooperation with the U. S. Geological Survey, is one step toward a complete geologic map of Tennessee. It contains 14 map sheets, size 20 by 26 inches, in color, on a scale of 1 to 125,000, and is accompanied by a larger folded sheet of sections. Explanatory text is to follow later. This is a fine piece of work to be undertaken by the state. Thee volume is bound, like a folio, and is nicely printed with good registration of colors.

BOOKS RECEIVED.

FRANK G. LESURE.

U. S. Geological Survey—Washington, D. C., 1952

Circ. 127. Geochemical and Mineralogical Methods of Prospecting for Mineral Deposits. TRANSLATED FROM RUSSIAN BY LYDIA HARTSOCK AND A. P. PIERCE. Pp. 37; tbls. 9. *Descriptions of certain geochemical methods and principles not widely applied outside of Soviet Union.*

Circ. 199. U. S. Geological Survey Fluorimetric Methods of Uranium Analysis. F. S. GRIMALDI, IRVING MAY, AND M. H. FLETCHER. Pp. 20; figs. 16; tbl. 1.

Circ. 212. Uranium-bearing Coal and Carbonaceous Rocks in the Fall Creek Area Bonneville County, Idaho. JAMES D. VINE AND GEORGE W. MOORE. Pp. 10; pl. 1; figs. 4; tbl. 1. *Uranium minerals believed absorbed by carbonaceous material from meteoric waters percolating down through overlying silicic volcanic source rocks.*

Circ. 214. The Occurrence of Zeaunerite at Brooks Mountain Seward Peninsula, Alaska. WALTER S. WEST AND MAX G. WHITE. Pp. 7; fig. 1; tbl. 1.

Circ. 217. Preliminary Report on the White Canyon Area San Juan County, Utah. W. E. BENSON, A. F. TRITES, JR., E. P. BERONI, AND J. A. FEEGER. Pp. 10; pl. 1; figs. 2. *Preliminary studies indicate a hydrothermal origin for copper-uranium minerals.*

U. S. Atomic Energy Commission—Oak Ridge, Tennessee, 1951–52.

RMO-912. Geological Investigation of the Trachyte District, Henry Mountains, Utah. GERALD L. BROOKE, RAYMOND F. SHIRLEY, AND MELVIN A. SWANSON. Decemebr 6, 1951. Pp. 6; figs. 2.

RMO-983. New Data of Syntheses of Uranium Minerals. Part I. Annual Report for July 1, 1951 to June 30, 1952. JOHN W. GRUNER. Pp. 26; tbls. 3.

Pleistocene Eolian Deposits of the United States, Alaska and Parts of Canada. JAMES THORP AND H. T. U. SMITH, Co-Chairmen. Geological Society of America, 1952. Price, $3.00. *Colored map in 2 parts, scale 1:2,500,000. Shows distributions of eolian silt (loess) and eolian sand and clay.*

The Composition and Assaying of Minerals. JOHN STEWART-REMINGTON AND WILFRED FRANCIS. Pp. 127. Price, 17/6d. *Includes methods of assays for the more important metals.*

California Division of Mines—San Francisco, 1952.

Publications of the California State Division of Mines. Pp. 120. *Contains complete list of publications to October 1, 1952.*

Special Rept. 20. Geology of the Superior Talc Area, Death Valley, California. LAUREN A. WRIGHT. Pp. 22; pl. 1; figs. 15. Price, 50 cents. *Talc deposits a result of contact metamorphism of Crystal Springs carbonates at or near diabase sill.*

Special Rept. 21. Geology of Burruel Ridge Northwestern Santa Ana Mountains, California. JAMES F. RICHMOND. Pp. 16; pl. 1; figs. 11. Price, 50 cents.

Special Rept. 22. Geology of Las Trampas Ridge, Berkeley Hills, California. CORNELIUS K. HAM. Pp. 26; pl. 1; figs. 20. Price, 50 cents.

Special Rept. 23. Exploratory Wells Drilled outside of Oil and Gas Fields in California to December 31, 1950. GORDON B. OAKESHOTT, LEWIS T. BRAUN, CHARLES W. HENNINGS, AND RUTH WELLS. Pp. 77; pls. 2. Price, $1.25; map alone, $1.00. *Lists location, name of company and well, date started and abandoned, total depth, and geology at bottom of wells drilled outside principal oil and gas fields. Includes outline geologic map showing oil and gas fields and drilled areas.*

Special Rept. 24. Geology of Lebec Quadrangle, California. JOHN C. CROWELL. Pp. 24; pls. 2; figs. 10. Price, 75 cents.

Special Rept. 25. Rocks and Structure of the Quartz Spring Area, Northern Panamint Range, California. JAMES F. MCALLISTER. Pp. 38; pls. 3; figs. 13. Price, 75 cents.

Special Rept. 26. Geology of the Southern Ridge Basin, Los Angeles County, California. PETER DEHLINGER AND CHARLES W. JENNINGS. Pp. 11; pl. 1; figs. 7. Price, 50 cents.

Colorado Bureau of Mines—Denver, 1952.

Report for the years 1950–51. Pp. 108.

State Geological Survey of Illinois—Urbana, 1952.

Illinois Petroleum No. 66. Illinois Oil-field Brines, their Geologic Occurrence and Chemical Composition. WAYNE F. MEENTS, ALFRED H. BELL, O. W. REES, AND W. G. TILBURY. Pp. 38; figs. 13. *Contains brine analyses for all producing pools in Illinois.*

Illinois Petroleum No. 67. Oil and Gas Development in Illinois During 1951. ALFRED H. BELL AND VIRGINIA KLINE. Pp. 54; figs. 2; tbls. 6. *Gives production, drilling, development and estimated reserves.*

Circ. 181. Mineral Resource Research and Activities of the State Geological Survey, 1951–1952. M. M. LEIGHTON, Chief. Pp. 58; figs. 23. *Annual report.*

State Geological Survey of Kansas—Lawrence, 1952.

Bull. 96, Part 7. Amenability of Certain Kansas Clays to Alumina Extraction by the Lime-Sinter Process. E. D. KINNEY. Pp. 308–328; figs. 3; tbls. 17. *Laboratory tests indicate that Kansas clays are amenable to treatment by lime-sinter process for use as high-alumina refractory material or as a source of aluminum ore.*

Bull. 99. Pleistocene Geology of Kansas. JOHN C. FRYE AND A. BYRON LEONARD. Pp. 230; pls. 19; figs. 17. *Detailed description of stratigraphy, molluscan fauna and drainage patterns.*

Summary of the California Company Thompson No. 1 Well, Bottineau County, North Dakota. DONALD TOWSE. Pp. 23. North Dakota Geol. Survey Circ. 7.

Ground-Water Levels in Ohio, 1949–1950. PAUL KASER. Ohio Division of Water, Bull. 25, Columbus, 1952. Pp. 103; figs. 147; tbls. 3. *Contains records of 201 wells.*

Pennsylvania Topographic and Geologic Survey—Harrisburg, 1952

Progress Rept. 140. The High Calcium Limestones of the Annville Belt in Lebanon and Berks Counties, Pennsylvania. CARLYLE GRAY. Pp. 17; pls. 2; figs. 6.

Bull. M 35. The Hyner and Ferney Anticlines and Adjacent Areas, Centre, Clinton and Lycoming Counties, Pennsylvania. JOHN R. EBRIGHT. Pp. 32; pls. 2; figs. 2. *Stratigraphy and structure of area southeast of Leidy gas field.*

University of Texas Bureau of Economic Geology—Austin, 1952.

Rept. of Inv. 14. Recognition of Hipparions and Other Horses in the Middle Miocene Mammalian Faunas of the Texas Gulf Region. JAMES HARRISON QUINN. and **New Paleocene and Lower Eocene Vertebrate Localities, Big Bend National Park, Texas.** JOHN A. WILSON, ROSS A. MAXWELL, JOHN T. LONSDALE, AND JAMES H. QUINN. Pp. 3.

Rept. of Inv. 16. High Purity Marble Falls Limestone, Burnet County, Texas. VIRGIL BARNES. Pp. 26; figs. 3; tbls. 3.

The Geology of Lost River State Park, West Virginia. JOHN C. LUDLUM. West Virginia Geol. Survey State Park Series Bull. 3, Morgantown, 1952. Pp. 33; pls. 21; figs. 3. *Popularized account for park visitors.*

Wyoming Mineral Resources. FRANK W. OSTERWALD AND DORIS B. OSTERWALD. Wyoming Geol. Survey Bull. 45, Laramie, 1952. Pp. 215; figs. 3. *Contains occurrences, production, and reserves of the metallic and non-metallic mineral resources.*

Canada Department of Mines—Ottawa, 1952.

Publications of the Geological Survey of Canada (1917–1952). Compiled by Lorne B. Leafloor. Pp. 82. Price, 50 cents.

Mem. 24. Carboniferous Stratigraphy and Paleontology on the Mount Greenock Area, Alberta. R. A. C. Brown. Pp. 119; pls. 5; figs. 16. Price, 75 cents.

Bull. 21. Ammonite Faunas of the Upper Cretaceous Rocks of Vancouver Island, British Columbia. J. L. Usher. Pp. 182; pls. 31; figs. 4; tbls. 3. Price, $1.00.

Ontario Department of Mines—Toronto, 1952.

60th Annual Rept., Vol. LX, Pt. VI, 1951. Geology of Errington Township, Little Long Lac Area. E. G. Pye. Pp. 140; pls. 34; figs. 26; tbls. 13. *Outlines stratigraphy and structure of area; describes mineralogy, origin and structural control of gold ore at various mining properties.*

60th Annual Rept., Vol. LX, Pt. VII, 1951. Geology of Harker Township. J. Satterly. Pp. 47; pls. 13; figs. 6. *Stratigraphy and structure of area. Description of gold deposits.*

60th Annual Rept., Vol. LX, Pt. VIII, 1951. Geology of Munro Township. J. Satterly. Pp. 60; pls. 26; figs. 4. *Stratigraphy and structure of area; description of asbestos and gold mining properties.*

Australian Bureau of Mineral Resources, Geology and Geophysics—Melbourne, 1952.

Quarterly Rev., Vol. 5, No. 1. The Australian Mineral Industry. Pp. 28. *Production statistics of important metallic and non-metallic minerals.*

Rept. 6. Geology of New Occidental, New Cobar and Chesney Mines, Cobar, New South Wales. C. J. Sullivan. Pp. 61; pls. 10; figs. 17; tbls. 13. *Description of structurally controlled copper-gold-silver deposits.*

Bull. 5. Australian Resources of Sulphur-bearing Minerals. P. B. Nye and G. F. Mead. Pp. 76; pls. 2; tbls. 31. *Description of sulphur-bearing mineral deposits including native sulphur, pyrite, pyrrhotite and mixed sulphides.*

Bull. 8. Ochre Deposits, Rumbalara, Northern Territory. C. J. Sullivan and A. A. Opik. Pp. 27; pls. 9; tbls. 3.

Pamph. 1. Production and Marketing of Mica. H. B. Owen and W. Turnbull. Pp. 15; pls. 2. *Notes for use of prospectors in Australia.*

Summary Rept. 2. Mineral Resources of Australia: Titanium (Rutile and Ilmenite). Pp. 36; figs. 3; tbls. 11. *Sources, production and consumption.*

Summary Rept. 29. Mineral Resources of Australia: Phosphates. Pp. 36; figs. 3; tbls. 14. *Sources, production and consumption.*

Report of the Geological Survey of Western Australia for the year 1949. Mines Dept. Annual Rept., Perth, 1951. Pp. 75; pls. 19; figs. 8. *Includes many short reports on metallic and non-metallic mineral deposits.*

Rapports et Bilans de l'exercice 1951. Comité spécial du Katanga, Bruxelles, 1952. Pp. 135; pls. 5; figs. 1; tbls. 7. *Annual report of the geographic and geologic service.*

Report of the Geological Survey Department for the Year 1951. British Territories in Borneo, Singapore, 1952. Pp. 143; pls. 6; figs. 19; tbls. 23. Price, Straits $3 or Sterling 7s. *Contains reports on gold, phosphates and coal deposits.*

Mineralogia, No. 9. Pp. 74; figs. 35. Bol. 147, Univ. de S. Paulo. S. Paulo, 1952. On the Chalcopyrite Inclusions in Sphalerite. WILLIAM G. R. DE CAMARGO. *Chalcopyrite inclusions believed result of exsolution;* Estudios sôbre as Propriedades Quimicas dos Minerais de Zircônio da Regiao de Poços de Caldas, Minas Gerais. WALTER LOEWENSTEIN. *Re-examination of zircon and ballelyite from Poços de Caldas with emphasis on hafnium content.*

Minerales, Ano VII, No. 41. Pp. 39–94. Santiago, 1952. *Papers on mechanization in small coal mines; new procedures in copper metallurgy; and geologic studies in Santiago province.*

I Giacimenti Piombo Zinciferi de Grigna e Pian da Barco nelle Alpi Orientali. DINO DI COMBERTALDO. Pp. 130; pls. 2; figs. 36. "Raibl," Soc. Mineraria del Predil, Roma, 1952. *Structure, petrography and mineralogy of lead-zinc ores near Mount Siarnola. Well illustrated with large composite microphotographs.*

Boletin del Centro de Documentacion Cientifica y Tecnica, Tomo I, No. 7. Pp. 1165–1408. Mexico, 1952. *A listing of important scientific papers including those from Latin America. To be published monthly with French or English abstracts for papers published in Latin America.*

The Greymouth Coalfield. MAXWELL GAGE. Pp. 232; pls. 24; figs. 32; tbls. 22. New Zealand Geol. Survey, Bull. 45, Wellington, 1952. Price, Text, £2 5s.; Maps, £1 15s.; both, £4. *Detailed stratigraphy and structure of cretaceous coal-measures and overlying Cenozoic sediments. Includes history and description of mines, coal reserves and prospecting recommendations.*

La Geographia del Nichelio. ELISEO BONETTI. Pp. 22; tbl. 1. Anno XXXII, No. 5, Trieste, 1952. *General discussion of occurrence and production of nickel.* Istituto Geografico Militare.

SOCIETY OF ECONOMIC GEOLOGISTS

PROGRAM OF ANNUAL MEETING TO BE HELD JOINTLY WITH THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS IN LOS ANGELES, CALIFORNIA, FEBRUARY 16–19, 1953.

TECHNICAL SESSIONS.

Monday, February 16, 1953.
9:45 A.M. to 12:00 noon.

Sierra Room, Ball Room Floor, Statler Hotel.

MINERAL DEPOSITS OF THE SOUTHWEST. I.

Chairmen: D. F. Hewett and Eldred D. Wilson.

1. Sketch of the geology and ore deposits of Baja California, Mexico. Edward Wisser, University of California, Berkeley, California.
2. Beryl deposits in the Harding pegmatites, Taos County, New Mexico. Richard H. Jahns, California Institute of Technology, Pasadena, California, and John W. Adams, U. S. Geological Survey, Denver, Colorado.
3. Economic geology of carbonatites associated with alkalic igneous rocks. William T. Pecora, U. S. Geological Survey, Washington, D. C.

Monday, February 16, 1953.
2:30 P.M. to 4:30 P.M.

Gallery, Mayfair Hotel.

MINERAL DEPOSITS OF THE SOUTHWEST. II.

Chairmen: George Tunell and Edward Wisser.

(PAPERS TO BE ANNOUNCED LATER.)

Monday, February 16, 1953.
2:30 P.M. to 4:30 P.M.

Buffalo Room, Ball Room Floor, Statler Hotel.

GEOLOGY AND PRODUCTION PROBLEMS OF DIMENSION STONE.

(Joint session with Industrial Minerals Division, A.I.M.E.)

Chairmen: Charles F. Deiss and Robert C. Stephenson.

1. Dimension stone industry of California. L. A. Norman, Jr., California Division of Mines, San Francisco, California.

2. A quarter century of granite quarrying in Massachusetts. Ralph E. Fletcher, H. E. Fletcher Company, West Chelmsford, Massachusetts.
3. Rock bursting and other geologic problems in the granite quarries at Barre, Vermont. Richard H. Jahns, California Institute of Technology, Pasadena, California.
4. Quarry practices in the Indiana building stone industry. Richard P. Letsinger, Victor Oolitic Stone Company, Victor, Indiana.
5. Stratigraphy and composition of the Salem limestone (Indiana building stone). John B. Patton, Indiana Geological Survey, Bloomington, Indiana.
6. Dimension stone in the United States in 1952—a summary. Charles F. Deiss, Indiana Geological Survey, Bloomington, Indiana.

Tuesday, February 17, 1953.

9:00 A.M. to 12:00 noon.

Rainbow Isle, Mayfair Hotel.

GEOLOGY AND TECHNOLOGY OF RARE-MINERAL DEPOSITS.

(Joint session with Industrial Minerals Division, A.I.M.E.)

Chairmen: Gordon H. Chambers and Richard H. Jahns.

1. The synthesis of industrial gems. Clifford Frondel, Harvard University, Cambridge, Massachusetts. (To be presented by Arthur Montgomery, Lafayette College, Easton, Pennsylvania.)
2. Monazite deposits of the Southeastern Atlantic States. John B. Mertie, Jr., U. S. Geological Survey, Washington, D. C.
3. Geochemical association of niobium (columbium) with titanium and its economic significance. Michael Fleischer, U. S. Geological Survey, Washington, D. C.
4. Minor-element accumulation in coal ash and its economic implications. Taisia Stadnichenko, U. S. Geological Survey, Washington, D. C.
5. Mining and milling of lithium pegmatites at Kings Mountain, North Carolina. E. R. Goter, W. R. Hudspeth, and D. L. Rainey, Foote Mineral Company, Kings Mountain, North Carolina. (To be presented by F. B. Shay, Foote Mineral Company, Paoli, Pennsylvania.)

Thursday, February 19, 1953.

9:00 A.M. to 12:00 noon.

New York Room, Ball Room Floor, Statler Hotel.

PANEL DISCUSSION ON NATURE AND ORIGIN OF ORE-FORMING FLUIDS.

Moderator: J. Hoover Mackin.

This session will comprise brief formal statements from the members of the panel, followed by informal discussion among members of the panel and the audience.

Thursday, February 19, 1953.

2:30 P.M. to 4:30 P.M.

Pacific Ball Room, Ball Room Floor, Statler Hotel.
GENERAL SESSION.

Chairmen: Eugene Callaghan and James A. Noble.

(PAPERS TO BE ANNOUNCED LATER.)

OTHER SESSIONS.

Monday, February 16, 1953.

A.I.M.E. Welcoming luncheon.

A.I.M.E. Stag Dinner—Smoker.

Tuesday, February 17, 1953.

A.I.M.E. Mining, Geology and Geophysics Division luncheon.

S.E.G. Annual Dinner and Presidential Address by Henry G. Ferguson.

Wednesday, February 18, 1953.

A.I.M.E. Industrial Minerals Division luncheon.

A.I.M.E. Annual Banquet.

SCIENTIFIC NOTES AND NEWS

THE KIRK BRYAN MEMORIAL AWARD has been established under the auspices of the GEOLOGICAL SOCIETY OF AMERICA by former students and other friends of the late PROFESSOR KIRK BRYAN. The award will consist of an inscribed certificate and a cash stipend for the encouragement of research, to be presented at annual meetings of the Geological Society, to the author or authors of outstanding contributions in geomorphology or in any one of the many bordering fields in which Professor Bryan was so actively interested. The award is to be based upon income from a Bryan Memorial Fund, administered by the Geological Society over a three-year period. $2,400 had been received for the fund by November 1, 1952, and an additional $1,940 has been pledged for gifts during the next two years. Further contributions may be sent to the Geological Society of America, 419 W. 117th Street, New York 27, ear-marked for the Bryan Memorial Fund.

SHRI S. K. BAROOH is now director of mines and geology at Naghpur, Central Provinces, India. He was previously located at Jodhpur.

After completing more than five years as chief geologist for Brazilian Traction Light and Power, PORTLAND P. FOX is returning to the United States in January. During his sojourn in Brazil, Mr. Fox explored and constructed two projects, Forcacava and Cubatao Underground Caverns, both of which are high heads for hydro plants, the first exceeding 1,000 feet and the second exceeding 2,200 feet. He expects to publish papers on each of these projects during the coming year. His address will be: c/o Dr. N. D. Fox, 1656 Reynolda Road, Winston Salem, N. C.

DR. M. WILLIAMS is now employed by the Consolidates Mining and Smelting Company at Kimberly, British Columbia, Canada. He had been with the Taquah and Abosso Mines, Ltd., at Abosso, Gold Coast, British West Africa, before making this change.

ROBERT C. STEPHENSON has recently resigned as Assistant State Geologist of Pennsylvania to accept a position in the mineral division of Woodward & Dickerson, Inc., Philadelphia, an import-export firm handling raw materials.

NEW YORK UNIVERSITY is offering a new course, called "Introduction to Economic Geography," for its adult evening study program during the Spring semester. Designed for persons without previous training in geography, the course will deal with material resources, industries and commerce and will be given by DAVID B. CHISHOLM, consulting geologist and assistant professor of geology and geography.

ALEXANDER DEUSSEN, consulting geologist of Houston, Texas, and HARRY R. JOHNSON, consulting geologist of Los Angeles, California, have been elected to honorary membership in the American Association of Petroleum Geologists. Only 16 other living geologists have been so honored during the 35-year history of the Association. Presentation of the coveted certificates of honorary membership will be given at the 1953 annual A.A.P.G. convention, to be held in the Sam Houston Coliseum, Houston, Texas, March 23–26.

J. A. RETTY, M.C.I.M., formerly Assistant to the President, Fenimore Iron Mines, Ltd., has been elected President of the Company, succeeding H. A. Strain, who becomes Chairman of the Board. Dr. Retty will continue to direct the company's exploration program.

J. J. O'NEILL, who retired recently as Vice-Principal of McGill University, has been designated an Honorary Life Member of the McGill Graduates' Society.

THE U. S. ATOMIC ENERGY COMMISSION has consolidated its exploration and procurement programs on the Colorado Plateau under an Operations Office at Grand Junction, Colorado under the management of SHELDON P. WIMPFEN, who has been assistant director of the Division of Raw Materials in Washington, reporting directly to Mr. Jesse L. Johnson. Mr. Wimpfen will assume his new duties on December 1, 1952.

THE NATIONAL SCIENCE FOUNDATION announces the appointment of a panel of specialists in geology, mining, and geophysics representing industry, government, and the universities to advise the National Science Foundation on policy questions connected with the recommendations for the President's Materials Policy Commission for development of the mineral resources of the United States. The first meeting of the panel was held in Washington on November 29, 1952. The advisory panel will consider the need for an inventory of current research in exploration and the formation of a committee to make such an inventory. The membership of the advisory panel includes the following: JOHN G. BARTRAM, consulting geologist, Stanolind Lil and Gas Company, Tulsa, Oklahoma; ALAN M. BATEMAN, Silliman professor of geology, Yale University, New Haven, Connecticut; JAMES BOYD, exploration manager, Kennecott Copper Corporation, New York City, and former director of the U. S. Bureau of Mines; ARTHUR H. BUNKER, president, Climax Molybdenum Company, New York City; PAUL D. FOOTE, executive vice-president, Gulf Research and Development Company, Pittsburgh, Pennsylvania; L. C. GRATON, professor of mining geology, Harvard University, Cambridge, Massachusetts; JOHN GUSTAFSON, M. A. Hanna Company, Cleveland, Ohio; THOMAS NOLAN, assistant director, U. S. Geological Survey, Washington, D. C.; LOUIS SLICHTER, director, Institute for Geophysics, University of California, Los Angeles, California; JOHN VANDERWILT, president, Colorado School of Mines, Golden, Colorado; CLYDE E. WILLIAMS, director, U. S. Geological Survey, Washington, D. C.; DONALD H. McLAUGHLIN, president, Homestake Mining Company, San Francisco, California, and member of the National Science Board; ANDREY A. POTTER, dean of engineering, Purdue University, Lafayette, Indiana, and member of the National Science Board; EARL P. STEVENSON, president, Arthur D. Little, Inc., Cambridge, Massachusetts, and member of the National Science Board; PAUL E. KLOPSTEG, assistant director, National Science Foundation, Washington 25, D. C.

THE SOCIETY OF EXPLORATION GEOPHYSICISTS held its sixth annual midwestern meeting in Ft. Worth, November 13–14, 1952, at which 23 papers were discussed.

ROBERT W. BRIDGEMAN, formerly with the U. S. Geological Survey and the State Department, is president of International Minerals Corporation of New York and Chester, Pennsylvania.

W. C. LACY, Chief Geologist of the Cerro de Pasco Corporation, is serving as lecturer in geology at Harvard University during the second half of 1952–53, replacing H. E. McKinstry who is on sabbatical leave.

FREDERICK M. CHANCE has joined the staff of Goldfields American Development Company.

FREDERICK C. KRUGER has left the University of Tennessee and is now with the Reynolds Mining Company whose headquarters are at Little Rock, Arkansas.

JOE VENUTO is now geologist with the New Jersey Zinc Company.

GEORGE S. KOCH has recently gone to Chihuahua as geologist for San Francisco Mines of Mexico.

G. C. CHERITON has completed his doctoral studies at Harvard University and has joined the Anaconda Copper Company as geologist.

RICHARD KIMBALL is with the Cerro de Pasco Corporation as geologist, presently located as Casapalca, Peru.